I

NUCLEAR MAGNETIC RESONANCE ANALYSIS OF FERROCENYLCARBONIUM ION

II

FERROCENE CATALYZED PHOTOCHEMISTRY

Thesis by

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ABSTRACT

I. Nuclear magnetic resonance spectra of appropriately substituted ferrocenylcarbonium ions reveal the α-protons of the substituted ring to be more shielded than the β-protons. The observation is discussed in terms of various models proposed for the ferrocenylcarbonium ion and is found to support a model in which the iron is bonded to all six carbons of the substituted ring.

II. Ferrocene catalyzes the photoisomerization of the piperylenes and the photodimerization of isoprene. Our results suggest a mechanism in which a complex of ferrocene and diene is excited to its second singlet state which dissociates to a triplet-state ferrocene molecule and a triplet-state diene molecule. The triplet-state diene, then, proceeds to isomerize or attack ground-state diene to form dimers.

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We shall not cease from exploration
And the end of all our exploring
Will be to arrive where we started
And know the place for the first time

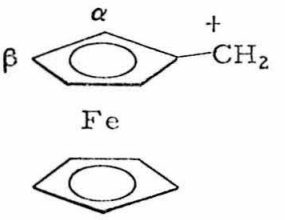
T. S. Eliot

PART I

Nuclear Magnetic Resonance Analysis of Ferrocenylcarbonium Ion

INTRODUCTION

Hill and Richards reported that ferrocenylcarbinyl carbonium ion, I, possesses extreme stability (1). For example, the solvolysis rate for ferrocenylcarbinyl acetate in 80% acetone/water is very



I

similar to the corresponding rate of solvolysis of trityl acetate (1). These authors attributed the unusual stability of I in part to interaction of the iron with the methylene carbon (2). Solvolysis rates of related, sterically constrained acetates, such as α-acetoxy-1,2-tetramethyleneferrocene are much larger for the exo- than for the corresponding endo-isomers (3, 4) and support the iron-stabilized carbonium ion model.

More recently, Ware and Traylor (5) have challenged the concept of iron participation in these carbonium ions. They argued that the solvolysis rates observed might be adequately explained by a carbonium ion model in which resonance interactions with the cyclopentadienyl ring account for virtually all of the charge stabilization transmitted to the methylene center.

Levenberg suggested that the α-ring protons of I might experience more magnetic shielding than the corresponding β-ring protons (6). A

careful study of the nuclear magnetic resonance spectra of ferrocenyl-carbonium ions might, therefore, provide useful information about the question of iron participation in these ions. Our results show that the α-protons do experience more magnetic shielding than the β-protons in these carbonium ions. These results are consistent with an iron-participation model for stabilization of the carbonium ion, and inconsistent with a resonance-stabilization model.

RESULTS

We sought to assign the proton resonances of the ferrocenyl carbonium ion, I, by analogy to the spectra of similar carbonium ions substituted in the α-position of the ring with a deuterium atom or a methyl group. Neither substitution should greatly affect the chemical shifts of the ring protons. The substituted and unsubstituted ring proton chemical shifts for methylferrocene are virtually identical, as can be seen from the n. m. r. spectrum of this compound (Fig. 1).

The method for specifically lithiating the α-position of ferrocenylcarbinyldimethylamine, II, developed by Slocum, Rockett, and Hauser (7), provided a convenient and unambiguous route for the synthesis of the substituted carbonium ions. The α-lithiated amine obtained by this procedure was either hydrolyzed with deuterium oxide and then treated with methyl iodide to yield α-deuteroferrocenylcarbinylmethylammonium iodide, IV, or treated with methyliodide directly to yield α-methylferrocenylcarbinyltrimethylammonium iodide, V. Basic hydrolysis of the ammonium iodides afforded the carbinols, VI and VII. The carbonium ions, VII and IX, were generated by dissolving the carbinols in either 98% sulfuric acid or in borontrifluoride monodeuterated (see Scheme I). Measurement of the freezing point depression of concentrated sulfuric acid upon dissolution of the carbinols indicated that four moles of ions are formed per mole of carbinol dissolved, (corresponding to one mole of ferrocenyl carbonium ion, one mole of hydronium ion and two moles of bisulfate ion), thereby con-

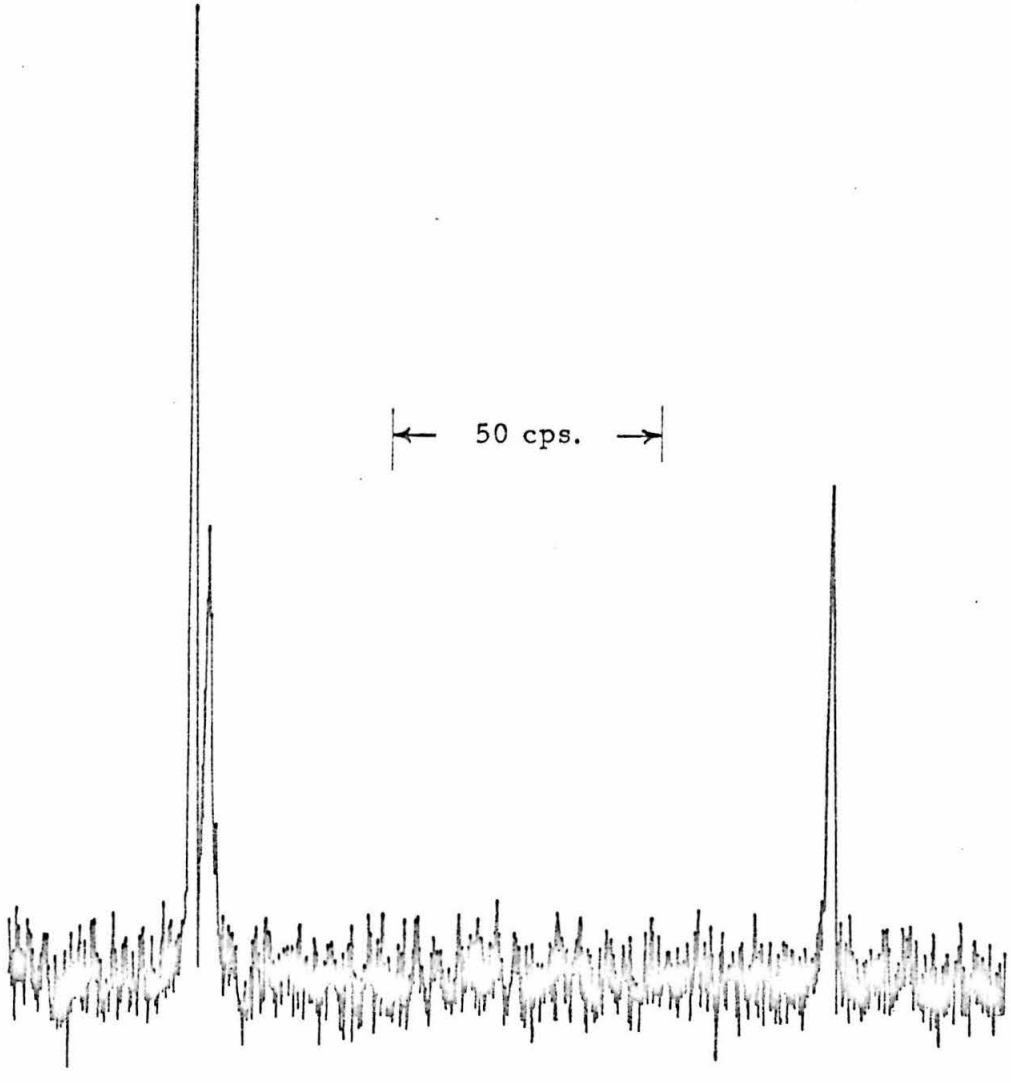
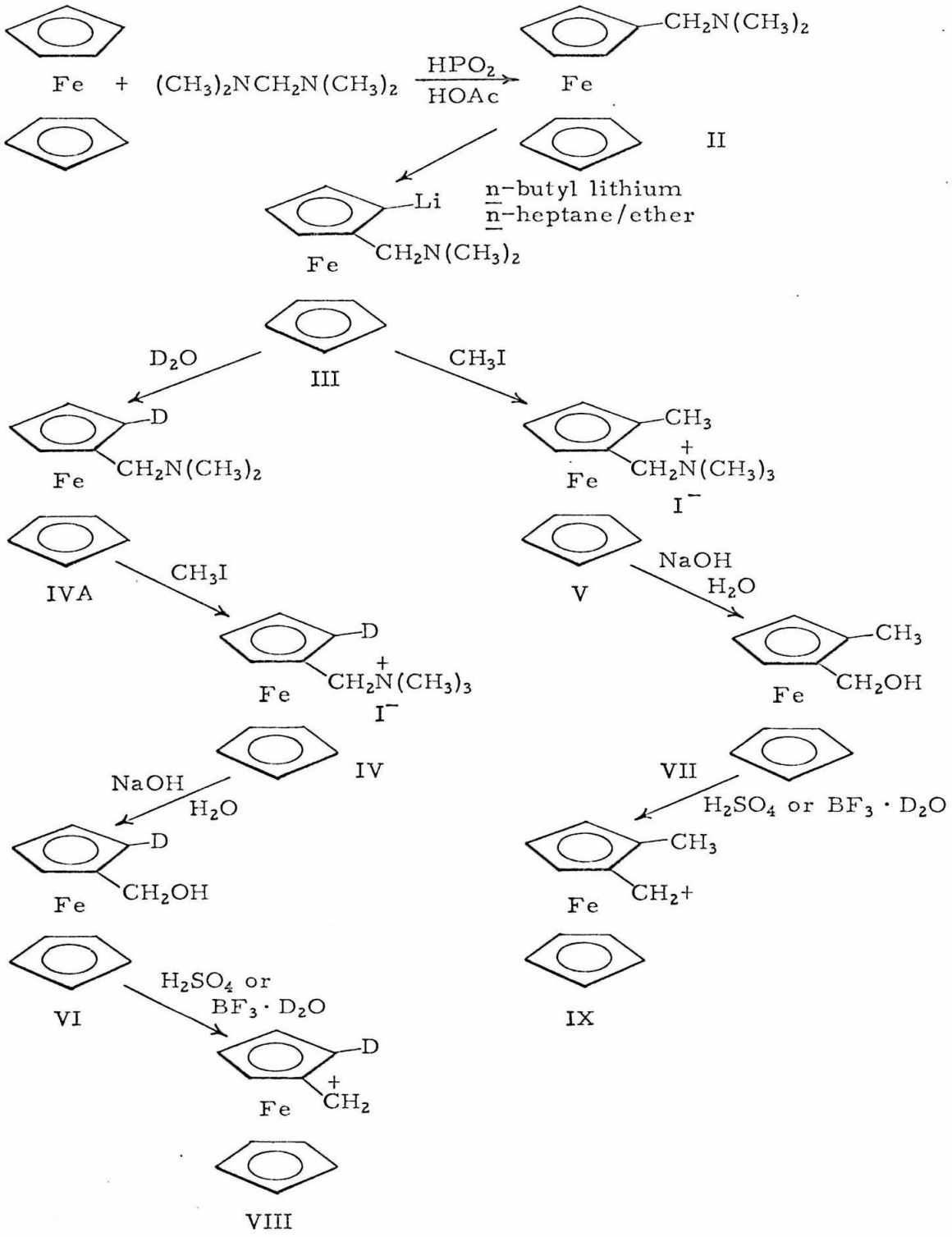


Figure 1. N. m. r. spectrum of methylferrocene.

Scheme I


Fe + (CH3)2NCH2N(CH3)2
HPO2
HOAc
CH2N(CH3)2
II
n-butyl lithium
n-heptane/ether
Li
III
D2O
CH3I
D
CH3
+
CH2N(CH3)3
I−
IVA
V
NaOH
H2O
CH2OH
IV
VII
H2SO4 or BF3 · D2O
CH2+
VI
IX
VIII

firming the existence of the free carbonium ion (6).

The n.m.r. spectra of the three carbonium ions, I, VIII, and IX are shown in Figure 2; the chemical shifts are listed in Table 1.

The n.m.r. spectrum of the sample of α-methylferrocenylcarbinol prepared by the above procedure shows that this sample is contaminated with a significant amount of the unsubstituted carbonium ion, I. Nevertheless, the spectrum of IX can be ascertained by subtracting the spectrum of I from the spectrum of the mixture. Integration of the unsubstituted ring peaks in the spectrum of the mixture indicates that the methylated carbonium ion accounts for 60-65% of the mixture. Integration of the substituted ring peaks of the deuterated carbonium ion, VIII, results in an α-proton : β-proton ratio of 1.37 : 2.0. This ratio, which corresponds to 60-65% deuteration, is not unexpected as both substituted carbonium ions were derived from the same lithiated intermediate, III.

The spectra of Figure 2 clearly indicate that the resonances at higher field are due to the α ring protons since these peaks decrease in intensity when deuterium is substituted for α-hydrogen. The β-proton resonances, manifest as a triplet in the spectrum of the unsubstituted carbonium ion, should exist as doublets in the α-substituted cases. A calculation of the resonances of the α- and β-protons using the coupling constants of Levenberg and Richards (8) and assuming that these protons couple only with each other, supports this expectation. The spectrum of the methylated carbonium ion, IX, in which the resonances of the β-protons are not obscured, shows a doublet for these resonances. Superposition of the doublet attributable to the

Figure 2. Spectra of a) a mixture of approximately 65% α-deutero-ferrocenylcarbinyl carbonium ion, 35% ferrocenylcarbinyl carbonium ion; b) ferrocenylcarbinyl carbonium ion; c) a mixture of approximately 65% α-methylferrocenylcarbinyl carbonium ion, 35% ferrocenylcarbinyl carbonium ion. All spectra were taken in concentrated sulfuric acid.

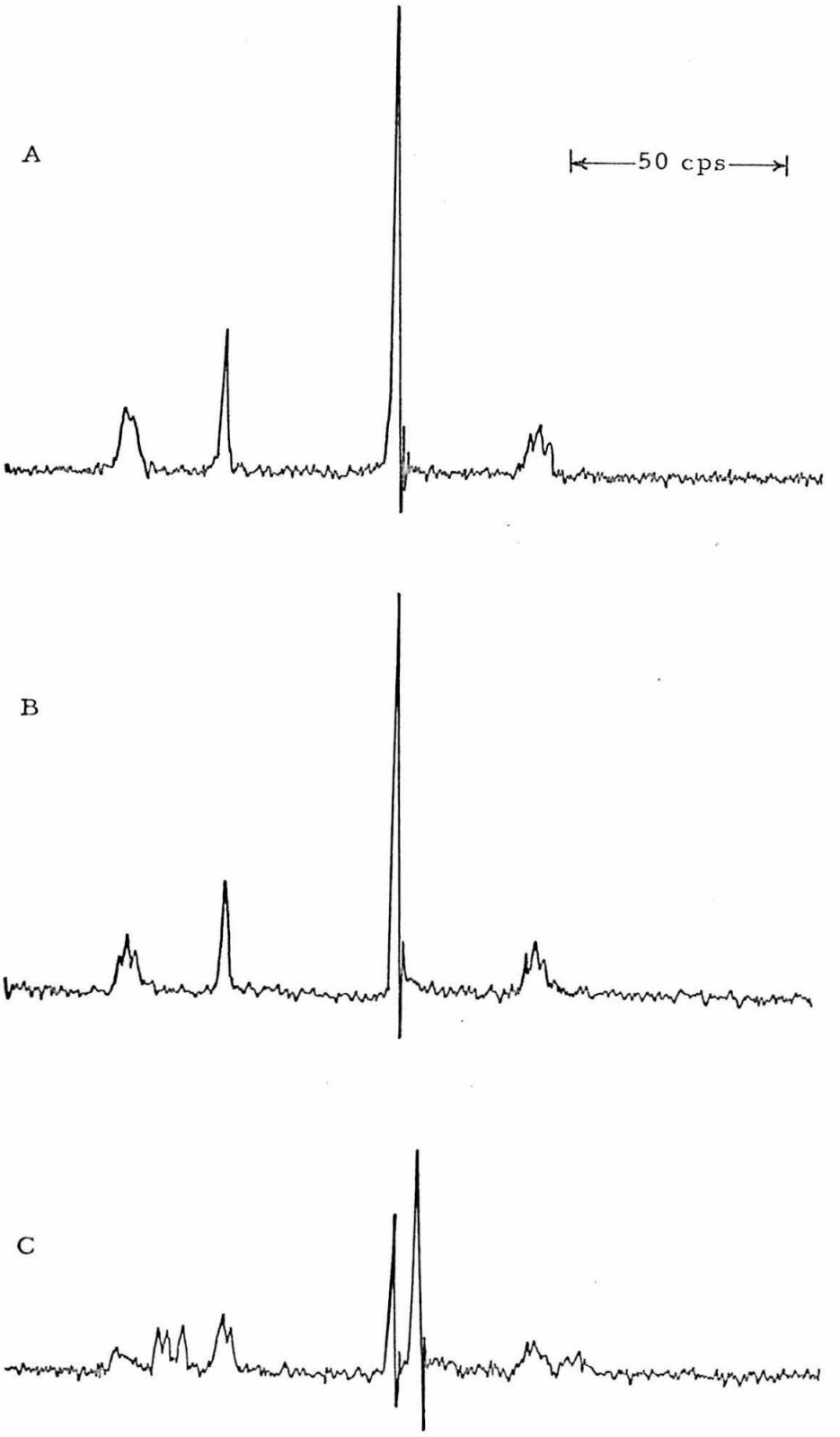
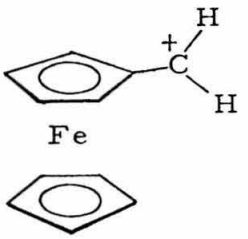
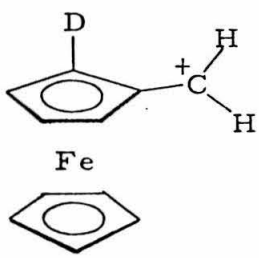
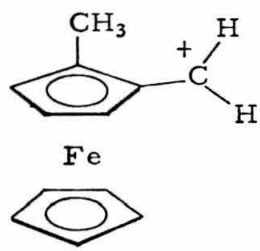

A
50 cps
B
C

Table 1

Chemical Shift Assignments of Ferrocenylcarbonium Ions

Carbonium Ion	Chemical Shifts			
	CH_2+	α–H	β–H	C_5H_5
	5.90	4.68 triplet	6.28 triplet	5.23
	5.90	4.68 triplet	6.28 doublet	5.93
	5.80, 6.12	4.51 triplet	6.13 doublet	5.03

The chemical shifts listed were measured using tetramethylammonium chloride (3.10 δ) as a standard. All shifts are in ppm. from tetramethylsilane.

β-protons of the deuterated carbonium ion upon the triplet attributable to the β-protons of the unsubstituted carbonium ion, with which VIII is contaminated, accounts for the unresolved multiplet observed for the β-protons of this mixture. The α-proton resonances of all three carbonium ions appear as triplets, as is also predicted by the aforementioned calculations. The resonances of the methylene protons are sharp singlets in the cases of both I and VIII. In the spectrum of IX, however, the methylene protons are not equivalent. Evidently, this non-equivalence is due to a large barrier to rotation about the bond between the cyclopentadienyl ring and the methylene group.

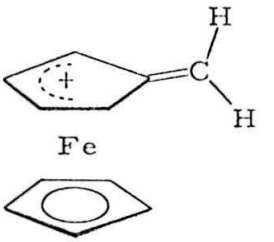
The low field lines in the spectrum if IX must be attributable to the two β-protons and the two methylene protons. We have assigned the two large lines at lowest field to the β-protons since the coupling between them is the same as the coupling between the lines of the α-proton triplet. The remaining lines correspond to the methylene protons which appear as an AB quartet. The higher field wing of the quartet is easily identifiable in Figure 2, while the lower field wing is partially obscured by the β-proton resonances of the unsubstituted carbonium ion I.

Although we do not have enough concrete evidence to determine which of the methylene protons is the more shielded, we have tentatively assigned the resonance at higher field to the methylene proton nearest the methyl group for reasons which are discussed below.

DISCUSSION

The Resonance Model

The resonance model for ferrocenylcarbonium ions, as proposed by Ware and Traylor (5), attributes the high degree of stability possessed by these ions to mesomeric interactions as depicted in X.



X

According to this model, the iron is in the same position relative to both rings. If this be the case, we anticipate the β-protons to be more shielded than the α-protons for the reasons outlined below.

Studies by Fraenkel, Carter, McLachlan, and Richards (9) and by Schaefer and Schneider (10) have demonstrated that the chemical shift of a hydrogen which is bonded directly to an aromatic ring is proportional to the negative charge density on the carbon to which it is bonded. As can be seen from Table 2, simple molecular orbital treatments predict that resonance interactions in a fulvene system (taken here as a first approximation to the substituted ring of I) which contains between five and six π electrons should cause the β-carbons to be negative with respect to the α-carbons. The correlation of calculated and observed chemical shifts for phenylcarbonium ion (11, 12) and phenylcarbanion (13) demonstrate the validity of a simple molecular

orbital theory approach to the calculation of the charge densities of Table 2. To whatever extent it must be added to the resonance effect, the inductive effect of the positive methylene group should also tend to

Table 2

Charges Calculated for α- and β-Protons of Fulvene Systems with Five and Six π-Electrons[a]

Electrons in System	Hückel Theory		Omege Technique[b]	
	α	β	α	β
5	.270	.065	.240	.110
6	-.092	-.073	-.074	-.045

a) See reference 14 for a description of the methods used.
b) Omega was taken as 1.0.

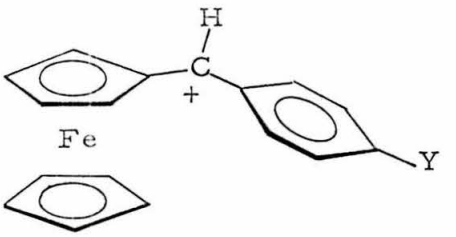
make the α-carbons more positive than the β-carbons. On the basis of charge densities, then, we expect the β-protons to be more shielded than the α-protons. Furthermore, the effect of the magnetic anisotropy of the double bond between the methylene carbon and the ring in X should also tend to deshield the α-protons more than the β-protons (15, 16).

The experimental n.m.r. spectra of ferrocenes which are substituted with an electron-withdrawing group typically exhibit α-proton resonances at lower field than β-proton resonances (17), in good accord with expectations based on the resonance model.

These arguments based on the resonance model for *ferrocenyl-*

carbonium ions lead to an incorrect prediction of the n. m. r. spectrum of I. We, therefore, conclude that such a model cannot accurately describe I.

Substituent effect studies (18) also accent the inadequacies of the resonance model. A correlation has been made between the methine proton chemical shifts and the substituent -Y for carbonium ions of the type XI (see Table 3). As -Y becomes more electron-withdrawing, the



XI

methine proton becomes more shielded, a result which is the opposite of that predicted by the resonance model.

Because the resonance model does not adequately account for the available n. m. r. evidence, let us reexamine the evidence which led Ware and Traylor to propose such a model to determine whether their evidence actually requires such a model or whether their evidence is merely consistent with this model.

The evidence cited in support of the resonance model involves: 1) Comparison of the effect of ferrocenyl and <u>para</u>-methyl substitution in the <u>para</u>-position upon the solvolysis rates of 1-phenylethyl chlorides, XII, with the effect of analogous substitution in the 1-position upon the solvolysis rates of ethyl chlorides, XIII; 2) correlation of the carbonyl stretching frequencies of the ketones XIV and XV, which correspond

Table 3

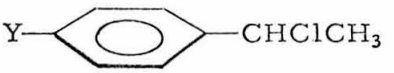
Chemical Shifts of Carbinyl Protons of Selected Cations

Cation	Chemical Shifts (ppm. from TMS)
ferrocenylcarbinyl	5.90
α-methylferrocenylcarbinyl	5.80, 6.12[a]
1-ferrocenylmethylcarbinyl	7.03[b]
ferrocenylisopropylcarbinyl	6.98[b]
ferrocenyl-t-butylcarbinyl	7.07[b]
ferrocenylphenylcarbinyl	7.92[b]
ferrocenyl-p-methylphenylcarbinyl	7.94[b]
ferrocenyl-p-methoxyphenylcarbinyl	7.96[b]
ferrocenyl-p-carbomethoxyphenylcarbinyl	7.67[b]
benzhydryl	9.80[c]
p-methoxybenzhydryl	9.06[b]

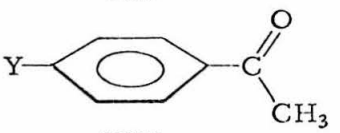
a) two nonequivalent protons, b) ref. 18, c) ref. 19

to these chlorides, with these solvolysis rates; and 3) comparison of the solvolysis rates of ortho-, meta-, and para-ferrocenyl-1-phenylethyl and ortho, meta, and para-methoxyl 1-phenylethyl chlorides. We shall consider each argument individually.

As one of the bases for their first argument, Ware and Traylor assumed the Hammett constant, ρ, for the solvolyses of 1-phenylethyl

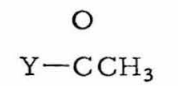


XII



XIV

XIII



XV

A, Y = ferrocenyl; B, Y = methoxyl; C, Y = H

chlorides to be identical to the corresponding constant for ethyl chlorides. They calculate ρ for these reactions to be -16 from equation 1, using a value of -0.78 for σ^+ p-methoxyl (20) and obtaining the solvol-

$$\log\left(\frac{k_{XIIIB}}{k_{XIIIC}}\right) \Big/ \sigma^{+}_{p\text{-}CH_3O} = \rho \qquad (1)$$

ysis rate constants from a table which they supplied (reproduced here as Table 4). Their value for ρ seems inordinately large for solvolyses of 1-phenylethyl chlorides. For example, ρ for the hydrolysis of benzyl chlorides in 47.7% ethanol at 30.4°C has been reported to be -2.178 (21). In fact, among 34 ρ values for solvolyses of related halides listed in a comprehensive review of substituent effects, the largest negative value to be found is -5.090 for the solvolysis of XVI in ethanol at

Table 4

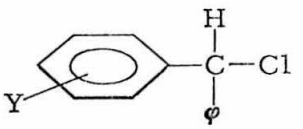
Relative Rates of Solvolyses of Chlorides at 25°*

Substituent	CH_3CHCl-	$CH_3CHClC_6H_4$
hydrogen	10^{-13}	1
ferrocenyl	1	–
methoxyl	>2	–
para-ferrocenyl	–	2.0×10^4
para-methoxyl	–	5.3×10^4

*from Ware and Traylor, reference 5.

25°C (21).

The value of ρ for 1-phenylethyl chlorides can be calculated from



XVI

equation 2. If one performs this calculation, again using the solvolysis rates of Table 4 and σ^+ p-methoxyl = −0.78, one determines ρ to be equal to −6, significantly different from the value of −16 obtained from

$$\log\left(\frac{k_{XIIB}}{k_{XIIC}}\right) \Big/ \sigma^+_{p\text{-}CH_3O} = \rho \qquad (2)$$

equation 1. We conclude that the assumption that the same ρ value is applicable to the solvolyses of both XII and XIII is clearly invalid. Consequently, equation 3, where this invalid assumption has been applied (5), cannot be expected to hold. In equation 3, $L_{ferrocene}$ represents the "anchimeric assistance provided by the non-bonding elec-

$$L_{ferrocene} = \log\left(\frac{k_{XIIIA}}{k_{XIIIB}}\right) + \rho\left(\sigma^+_{p\text{-}CH_3O} - \sigma^+_{p\text{-ferrocenyl}}\right) \qquad (3)$$

trons on iron," and $\sigma^+_{p\text{-ferrocenyl}}$ is calculated to be −0.71 from the data in Table 4, presumably by applying equation 4. Using this relationship, Ware and Traylor found $L_{ferrocene}$ to be less than or equal to 0.8, which corresponds to a six-fold rate enhancement in a total rate enhancement of 10^{13}.

$$\mathrm{Log}\left(\frac{k_{p\text{-}CH_3O}}{k_{p\text{-ferrocenyl}}}\right) = \frac{\sigma^+_{p\text{-}CH_3O}}{\sigma^+_{p\text{-ferrocenyl}}} \qquad (4)$$

The second argument presented in support of the resonance model is that the logarithms of the solvolysis rates of XIIA, XIIB, XIIC, and XIIIA can be linearly correlated with the carbonyl stretching frequencies of XIVA, XIVB, XIVC, and XVA (see Fig. 3). Both Foote (22) and Schleyer (23) have suggested that in cases where such a relationship holds, anchimeric assistance to carbonium ion formation is not important. However, the theory upon which the correlation is based pertains to bond angle and strain differences rather than electron density differences (22, 23). Although the benzyl substituent fits Foote's linear relationship quite adequately, the author comments (22):

> "It should be noted that although both polar substituents and conjugation affect rate and carbonyl frequency in the same way as angle strain (increased rates corresponding to decreased carbonyl frequencies), it is not clear that the relative effect would necessarily be of the same magnitude for angle strain."

Therefore, the linear relationship between carbonyl stretching frequency and log of solvolysis rates discussed by Ware and Traylor does not have a precedent in Foote's work and still awaits experimental verification. Also, Ware and Traylor did not include the carbonyl stretching frequency of one of the compounds with which they should have been concerned, XVB, in Figure 3. The stretching frequency for XVB (which is an ester) occurs at 1750 $cm.^{-1}$ (24). If plotted against the corresponding solvolysis rate for XIIIB, it would fall extremely far off the straight line of Figure 3.

Recently, Cais and Belanic-Lipovac have ascertained that no linear relation exists between the solvolysis rates of sbustituted ferrocenyl carbinyl acetates, XVII, and the stretching frequency of the

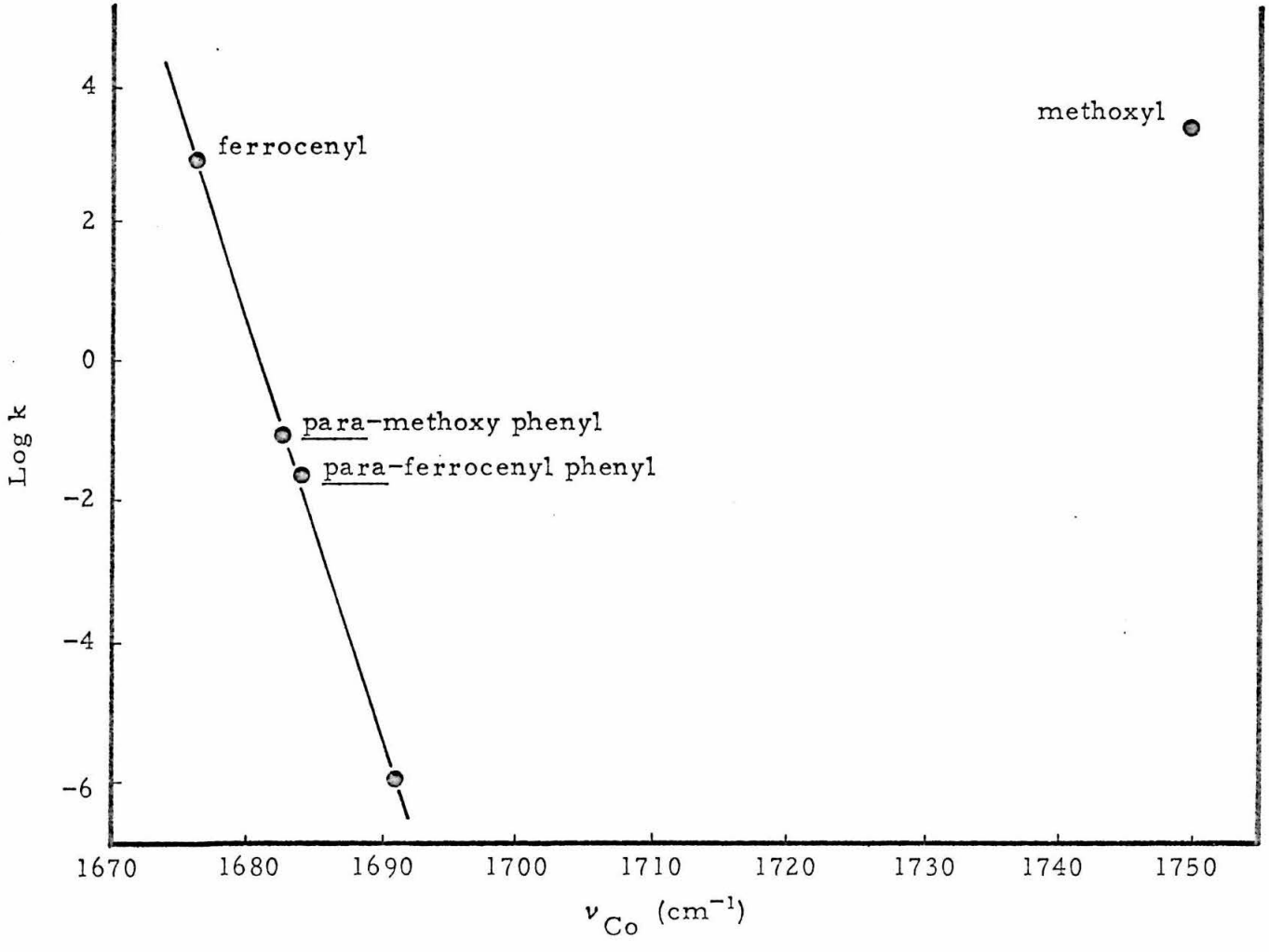
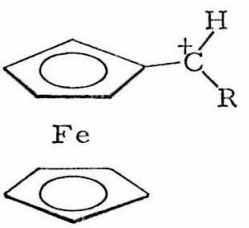
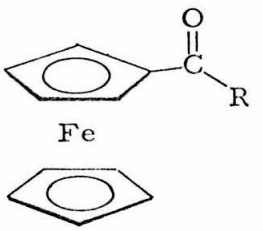


Figure 3. Plot of log of solvolysis rate constant of CH_3CHClR against the carbonyl stretching frequencies of CH_3COR in carbon tetrachloride. Points falling on the line are from a similar plot in reference 5. Methoxyl point uses rate constant of reference 6, stretching frequency of reference 24.

corresponding ketones XVIII, (25). Although the solvolysis rates of the acetates studied do not extend over so large a range as those studied by Ware and Traylor (5), the deviation from linearity observed by Cais is much larger than that observed by Traylor. We may conclude that



XVII



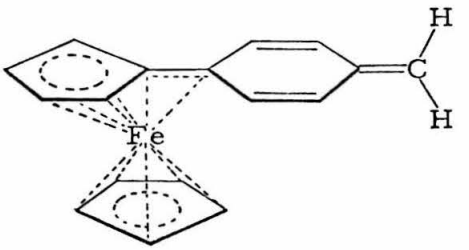
XVIII

R = phenyl,
p-methoxyphenyl,
p-carbomethoxyphenyl,
p-methylphenyl,
isopropyl

the relationship of Figure 3 does not require a resonance model.

The third argument, called "less conclusive" by its proponents, suggests that 1-ortho-ferrocenylphenylethyl chloride ought to be able to sterically allow iron participation at the carbonium ion site if it twists. Therefore, if this type of participation be important, the ortho-chloride should solvolize more rapidly than the corresponding meta- and para-chlorides. The discussion below should establish that iron participation, as we conceive it, does not involve the type of interaction that would be made possible by twisting the ortho-chloride. Rather, we expect the methylene group in I to be coplanar with and conjugated to the substituted ring.

Curiously, even if all of the data advanced in support of the resonance model were valid, this data could not eliminate the possibility of iron participation into the phenyl ring as depicted in XIX. Such a form of participation would be entirely analogous to the type of iron participation we propose for I.

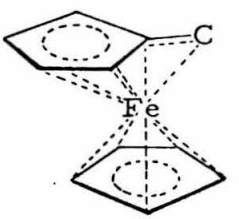


XIX

We conclude that the resonance model for the ferrocenylcarbonium ion is inaccurate since such a model cannot explain the n. m. r. data, and the evidence which has been advanced to support this model does not seem conclusive.

The Iron Participation Model

The manner of iron participation which we envision is that depicted in XX, in which the substituted ring is planar and conjugated as in fulvene. The iron is shifted somewhat away from the center of the



XX

substituted ring in the direction of the methylene group and the unsubstituted ring is symmetrically positioned relative to the iron, but is shifted (with the iron) relative to the substituted ring. Such a model readily accounts for the n. m. r. data. If the iron is positioned as in

XX, it should be nearer and therefore more closely bonded to the α-carbons than the β-carbons. Hence, we expect the positive charge on the α-carbons to be more stabilized by the iron than that on the β-carbons.

The magnetic anisotropy of unsymmetrical atoms, such as iron, can affect the magnetic environment of neighboring atoms, thereby influencing the chemical shifts of nearby protons (26, 27). For the case of unsubstituted ferrocene, the effect of the iron anisotropy upon the protons has been estimated to increase their chemical shift (δ) by 2.16 ppm (6). As the protons are moved nearer to the Z-axis of the iron (the rotational axis of ferrocene) the anisotropic shielding should increase. In XX, then, the α-protons should be more shielded by the anisotropic effect of the iron than the β-protons.

Finally, the ring current of the unsubstituted ring should exert an anisotropic effect qualitatively similar to (28) but of smaller magnitude (6) than the anisotropic effect of the iron. This effect, then, would also cause the α-protons to be more shielded than the β-protons in XX.

The three effects discussed above all additive and each would cause the α-protons to become shielded relative to the β-protons. These effects thus offer an explanation for the observed n. m. r. spectrum of ferrocenylcarbonium ion and also of the observed substituent effects on the methine resonance in XI. When an electron-donating group is in the para-phenyl position of XI, the charge on the methine carbon is more effectively stabilized by interactions with the phenyl part of the molecule than if the para-substituent of the benzene ring be

electron-withdrawing. In the former case, the iron need not stabilize as much positive charge as in the latter case. Since the iron loses bonding energy with the β-carbons by moving toward the methine position, it should move farther toward the methine carbon as the para-phenyl substituent becomes more electron-withdrawing. In other words, the potential energy surface of the carbonium ion is at a minimum with the iron less shifted from its "normal" position when the para-phenyl substituent is electron-donating. Charge stabilization is only one of the three ways in which the iron shields the methine proton since all of the above arguments concerning the shielding of the α-protons apply to the methine protons as well. The methine proton, consequently, is not as well shielded by the anisotropic magnetic fields of the iron and the unsubstituted ring when the charge is partially stabilized through the phenyl ring and these effects of magnetic anisotropy dominate effects due to charge density. This interpretation is in good agreement with the experimental results of Table 3.

We anticipate that an increase in the electron-donating capacity of the substituted phenyl ring in XI should have a greater effect upon the amount of iron shift when the potential minimum requires that the iron be significantly shifted than when the iron is near its symmetrical ferrocene position. In other words, the change in chemical shift per unit of electron-withdrawing capacity $\frac{d\delta}{d\sigma^+}$ is not linear and should increase as σ^+ increases. Figure 4 demonstrates that this anticipated relationship is valid.

An analogous explanation accounts for the observed decrease in shielding of the average of the methylene protons of IX relative to I

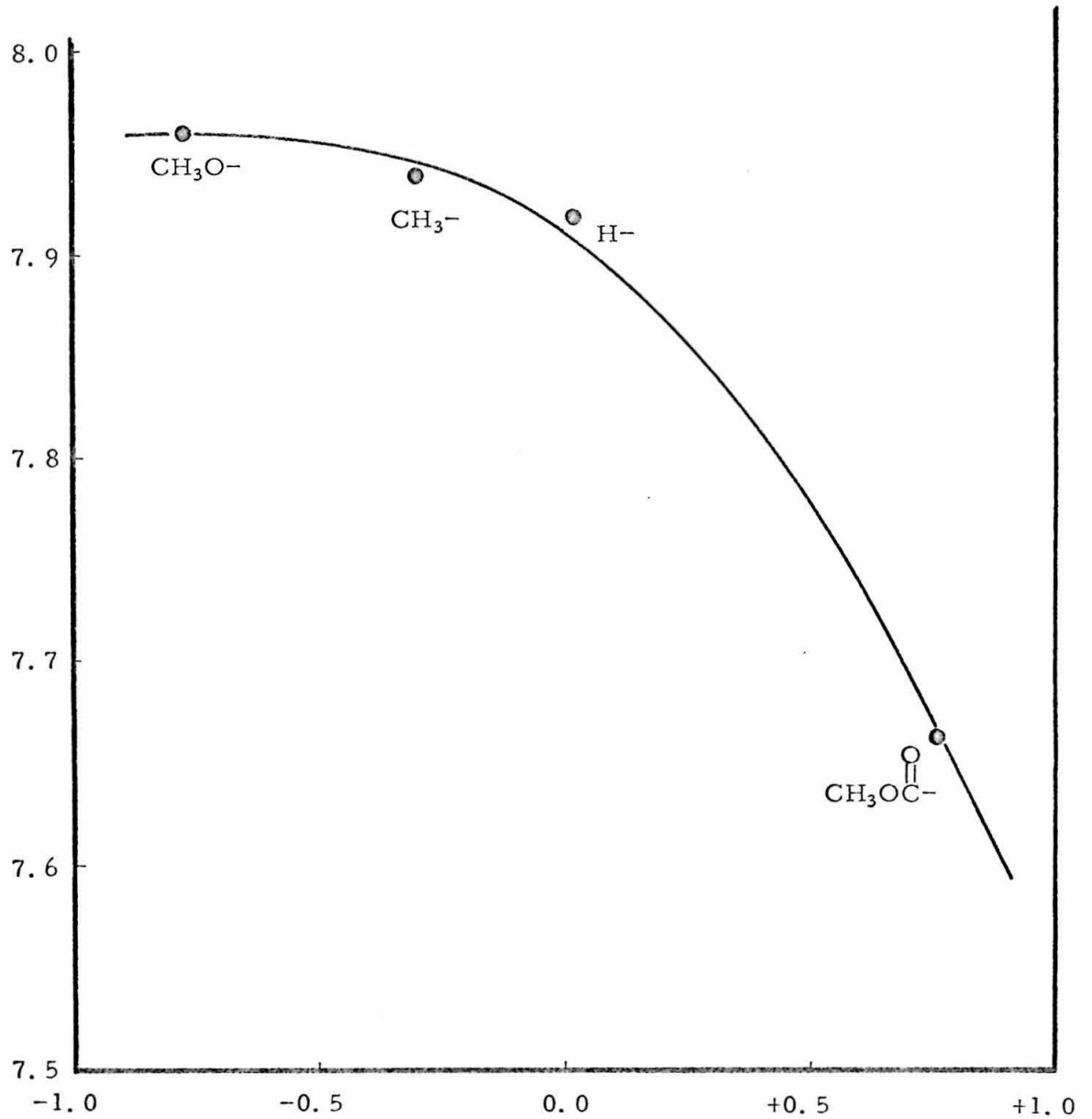


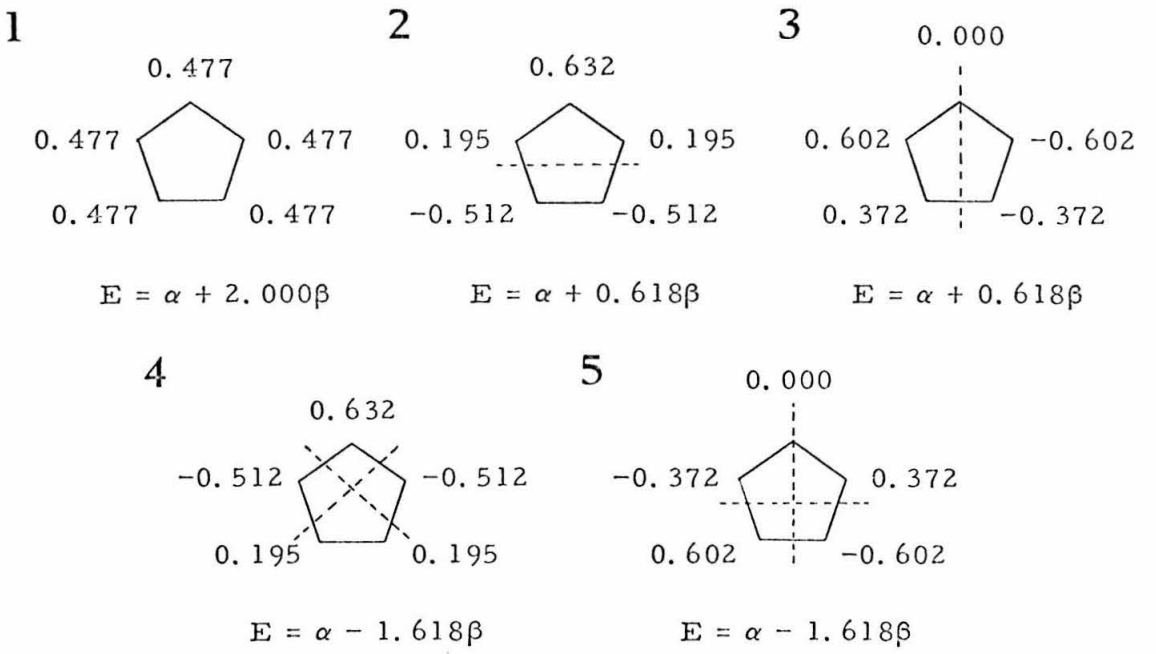
Figure 4. Plot of chemical shifts of para-substituted phenylferrocenylcarbonium ions, XI, against σ^+ and σ^- values of the para-substituents.

and XIII mentioned previously. The α-methyl group increases the amount of resonance stabilization of the methylene carbon that is conducted through the cyclopentadienyl ring, thereby decreasing the distance the iron must move to reach a potential minimum.

In terms of molecular orbital theory, we can consider ferrocene as two cyclopentadienyl entities which are bonded to an iron by means of interactions of the cyclopentadienyl molecular orbitals with the iron orbitals of the same symmetry (29). Analogously, we imagine the carbonium ion, I, to be described as one cyclopentadienyl and one fulvene entity bonded to an iron by means of similar interactions. The Hückel molecular orbitals for cyclopentadienyl and fulvene are shown in Figure 5 (30). All of the cyclopentadienyl orbitals are of proper symmetry for bonding with the iron 3d, 4s, and 4p orbitals (29). The fulvene orbitals numbered 1, 2, 3, and 5 have the same symmetry as the cyclopentadienyl orbitals numbered 1, 2, 3, and 5 in Figure 4. The centers of fulvene orbitals 1 and 2 lie to the methylene side of the center of the ring. These orbitals should stabilize the shifted iron of XVIII.

Other Models

Recently, two other models have been proposed for I. One is related to the resonance model and the other to the iron-participation model. The former was proposed by Pettit (31) at a recent seminar. He envisions XXI as the structure of cyclobutadienyl iron tricarbonyl carbonium ion and XXII as the likely structure for ferrocenylcarbonium ion I by analogy. In these structures, the iron has shifted away from



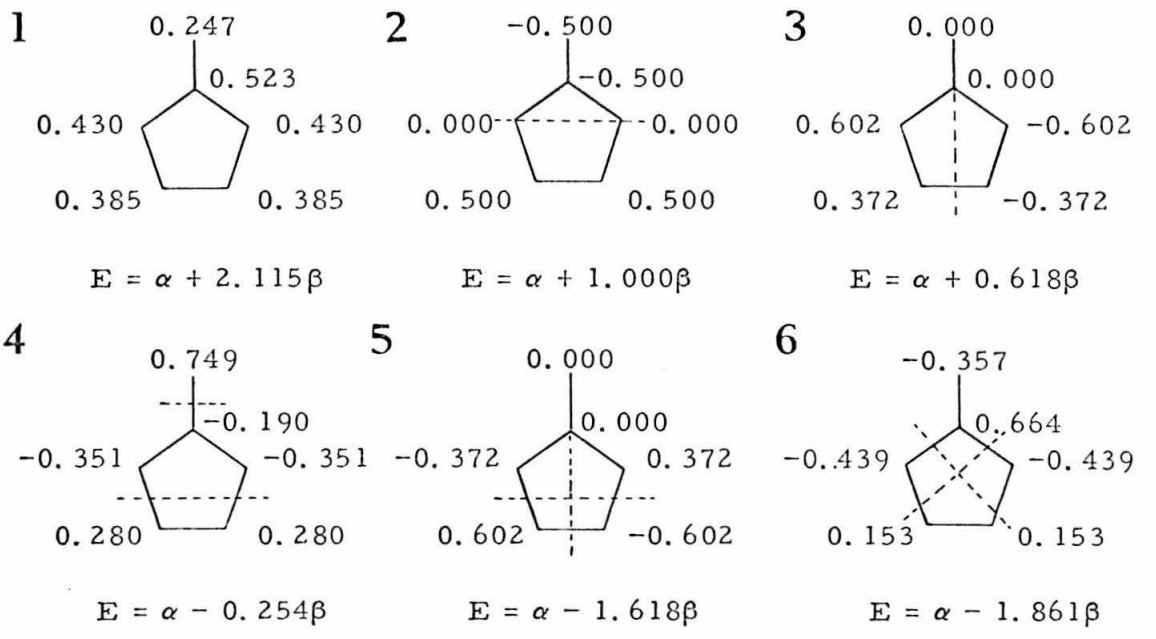
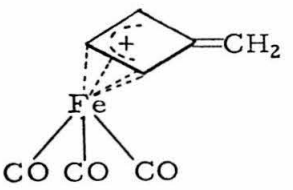
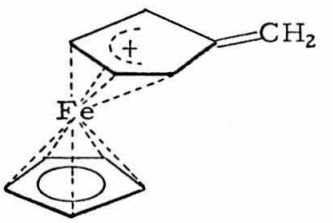


Figure 5. Hückel Molecular Orbitals for Cyclopentadienyl and Fulvene (30).

the methylene group and bonds only to the four carbons as in a diene complex. The n. m. r. spectrum of XXI is similar to that of I in that the α-protons are at higher field than the β-protons. Pettit explains

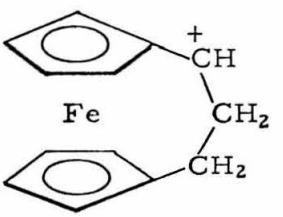


XXI

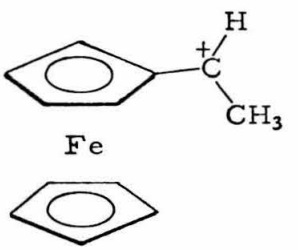


XXII

the relative shieldings of the α- and β-protons of I by analogy to diene iron tricarbonyl complexes, in which the terminal protons of the diene system resonate at fields approximately 2-4 ppm. higher than the central protons (32). The model depicted by XXII, however, would predict the same <u>para</u>-substituent effects upon the chemical shift of the methine proton of XI as does the resonance model. Also, the iron participation model would predict that the carbinyl proton of the bridged carbonium ion, XXIII, should be less shielded than the carbinyl proton of methyl-



XXIII



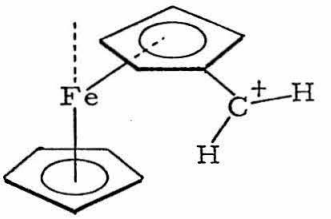
XXIV

ferrocenyl carbonium ion, XXIV, since the bridge in XXIII should hinder the shift of the iron toward the methine carbon. However, move-

ment away from the methine carbon, as proposed by Pettit, is not hindered in XXIII; therefore, if we can assume that the strain of the bridged sp^2 methine carbon does not appreciably affect the attached proton, Pettit's model would predict the chemical shift of the methine proton of XXI to be similar to that of XXIV. Experimental measurements indicate that the chemical shift of XXIII is 8.16 δ (33) and that of XXIV is 7.03 δ (Table 3), in good agreement with the iron participation model and not with Pettit's model.

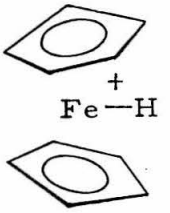
Pettit's model would also be hard to rationalize from a molecular orbital approach. The supposed reason that iron bonds only to two double bonds at a time in systems such as tropyllium iron tricarbonyl cation is that bonding to the entire π-system would require iron to coordinate more than the noble gas number of electrons (34). Such is not the case in I, where iron would have the krypton configuration if the fulvene system were considered to contain five electrons. In Pettit's model, XXII, iron coordinates only sixteen electrons. Although a group of iron π-complexes, the allylic iron tricarbonyl salts (35) have been reported, they decompose in aqueous solution, indicating that they are probably less stable than the eighteen electron π-complexes.

The other model recently proposed for I brings the iron closer to the methylene by rotating the substituted ring through an axis that passes through the iron and is parallel to the planes of the rings as in XXV (33). In such a system, the iron anisotropy should tend to shield the β-protons in preference to the α- and methylene protons (26, 27). We also find XXV hard to rationalize in terms of molecular orbital theory. There are two analogies in the ferrocene literature. One is a



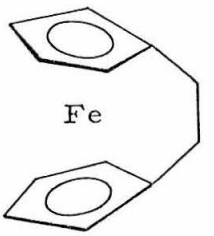
XXV

proposed structure for protonated ferrocene in which the rings are twisted away from the proton, XXVI (36). The iron orbitals of protonated ferrocene might be expected to rehybridize in order to provide a suitable orbital to bond the proton. In XXV, however, this type of symmetry is not possible because the methylene group cannot both occupy a position analogous to the proton bonded to iron in XXVI and remain bonded to the ring of XXV. The other analogy is 1, 1'-dimethyleneferrocene, XXVIII, where the dimethylene bridge strains the molecule, forcing the rings to twist (37). Whereas in the n. m. r. spectrum



XXVI

of 1, 1'-diisopropylferrocene all of the ring protons have about the same chemical shift, the ring protons of XXVIII are manifest as two triplets separated by 0. 86 ppm. (37). The iron anisotropy may, by selectively shielding the β-protons, which are situated more directly above and below the iron than are the α-protons, be responsible for the



XXVIII

observed difference in chemical shift. However, the α- and β-proton resonances of XXV have not been unambiguously assigned. We feel that the previously mentioned fact that the carbinyl proton of the bridged carbonium ion XXIII is much less shielded than the corresponding proton of XXIV provides evidence against this last model as does the fact that the corresponding bridged acetate solvolyzes more slowly by a factor of thirty than does 1-ferrocenylethyl acetate (1). Since the rings of the bridged acetate are probably twisted in a manner analogous to XXV, one might expect the ground-state energy of the bridged acetate to be higher than that of 1-ferrocenylethyl acetate; therefore, if the transition-state energies be the same for both α-acetoxy-1,1'-trimethyleneferrocene and 1-ferrocenylethyl acetate, the bridged acetate might solvolyze more rapidly. If the intermediate carbonium ion be twisted as in XXV, the transition state energies for the two solvolyses should be similar as assumed above. If, on the other hand, the transition state be not twisted, the transition state of the bridged acetate should be much more energetic than the transition state of 1-ferrocenylethyl acetate and the bridged acetate should solvolyze more slowly as observed. Moreover, the transition-state energy of the bridged acetate

should be somewhat greater than that of the 1-ferrocenylethyl acetate even if the carbonium ion be twisted as in XXV because the 1-ferrocenylethyl cation probably can more easily attain a planar sp^2 configuration about the carbinyl carbon than can the bridged carbonium ion. Since accurate estimations of the differences in both the ground states and transition states of these two acetates are not available, and the difference in the rates of solvolysis of the acetates is not extremely large, we hold this last argument to be indicative rather than conclusive.

EXPERIMENTAL

Ferrocenylcarbinyldimethylamine, II: Ferrocene (46 g., 0.25 mmoles) was added slowly to a mixture of 43 g. bis(dimethylamino)-methane (see below), 54 g. phosphoric acid and 400 ml. acetic acid in a 1-liter, 3-neck, round-bottom flask equipped with a magnetic stirrer, nitrogen inlet, and a condenser. The flask was heated and kept between 100 and 110°C. for 8-1/4 hours. The reaction mixture was then diluted (in two parts) with 500 ml. of water and extracted with ether to remove the excess ferrocene. The water layer was neutralized with 246 g. of sodium hydroxide pellets (added slowly, with stirring). The resulting semisolid was considerably diluted with water and then extracted with ether three times. The ether extracts were combined, dried over magnesium sulfate, and evaporated to leave a red oil. The oil was distilled. The fraction which boiled 89-96°/0.5-0.25 mm. mercury was collected and stored under nitrogen in the refrigerator.

The bis(dimethylamino)methane used in this synthesis was prepared by hydrolyzing an aqueous solution of 123 g. dimethylamine hydrochloride with an aqueous solution of 60 g. sodium hydroxide. The resulting dimethylamine solution was added slowly to 65 ml. of a 37% aqueous formaldehyde solution, cooled in an ice bath. The temperature was kept below 15°C. The reaction was stirred in an ice bath for 45 minutes. Then, 150 g. potassium hydroxide was added in five portions. The reaction mixture separated into two layers. The upper layer was collected and distilled from potassium hydroxide pellets. The fraction

distilling between 80-86°C was used for further reactions.

α-Lithioferrocenylcarbinyldimethylamine, III: Ferrocenylcarbinyldimethylamine, III, (2.44 g., 0.01 moles) and 10 ml. anhydrous ether (fresh can) were added to a 25 ml., 3-neck, round-bottomed flask fitted with a condenser, nitrogen inlet, and a dropping funnel. The system was flushed with nitrogen. Eight ml. 15% n-butyllithium in heptane (Foote, lot #401-02) was added dropwise through the dropping funnel. The reaction mixture was allowed to stand one hour under nitrogen. The solution was then used directly. This preparation affords only the α-lithiated compound, III. (7)

α-Deuteroferrocenylcarbinyldimethylamine, IVA: To the solution of α-lithioferrocenylcarbinyldimethylamine, III, described above was added dropwise approximately 2 ml. deuterium oxide. When reaction no longer occurred upon the addition of more deuterium oxide, water was added and the mixture extracted with ether. The ether layer was collected, dried over anhydrous magnesium sulfate, evaporated to yield IVA (7).

α-Deuteroferrocenylcarbinyltrimethylammonium iodide, IV: Unpurified α-deuteroferrocenylcarbinyldimethylamine, IVA, was dissolved in 15 ml. methanol. After cooling, 2-1/2 ml. methyl iodide was added. The mixture was refluxed for 2-1/2 hours. Upon addition of ether, a precipitate formed. This precipitate was collected and washed with ether. Yield: 2.43 g. IV.

α-Deuteroferrocenylcarbinol, VI: To 20 ml. of a 1 M aqueous

solution of sodium hydroxide in a round-bottomed flask flushed with nitrogen, was added 2.0 g. α-deuteroferrocenylcarbinyltrimethylammonium iodide, VI. The mixture was refluxed under nitrogen for two hours. The reaction mixture was then extracted with ether. The ether extract was washed with water until it became neutral, dried over anhydrous magnesium sulfate, and evaporated. The resulting solid was recrystallized from n-heptane.

α-Methylferrocenylcarbinyltrimethylammonium iodide, V: Five ml. methyl iodide was added dropwise to a solution of α-lithioferrocenylcarbinyldimethylamine, IV, as described above. Methanol was added to dissolve as much of the reaction mixture as was possible. The methanol solution was decanted from the solid. A large quantity of ether was added which caused the formation of a precipitate. The precipitate was collected and washed with ether. Yield: 2.8 g. VII, m.p. 170-5° decomp.

α-Methylferrocenylcarbinol, VII: To 20 ml. of a 1 M aqueous solution of sodium hydroxide in a round-bottomed flask was added 2.0 g. α-methylferrocenylcarbinyltrimethylammonium iodide, V. The mixture was refluxed for two hours. The reaction mixture was extracted with ether. The ether was washed with water until it became neutral, dried over anhydrous magnesium sulfate, and evaporated, leaving a red oil. An n.m.r. spectrum of the oil showed it to be a mixture of VII and of ferrocenylcarbinol.

Carbonium ions: Carbonium ions were prepared by dissolving

the carbinol in concentrated sulfuric acid. Deep red solutions were immediately formed. Occasionally, a brown or green solution formed, indicating that some oxidation had occurred. Oxidation was minimized by pre-chilling the sulfuric acid and the mixing vessel and by flushing the mixing vessel with nitrogen.

N. m. r. Spectra: The spectra were taken with the aid of a Varian A-60 nuclear magnetic resonance spectrometer immediately after preparation of the carbonium ions. Sulfuric acid was used as the n. m. r. solvent, and tetramethylammonium chloride as a reference (3. 10 δ).

Calculated n. m. r. transitions were obtained with the aid of the computer program written by Ferguson and Marquardt (38). All computations were carried out on IBM 7094 digital computer.

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PART II

Ferrocene Catalyzed Photochemistry

INTRODUCTION

Ferrocene catalyzes the photochemical cis-trans isomerization of the piperylenes and the dimerization of isoprene. The available evidence suggests that the mechanism for the photoisomerization involves a complex of ferrocene and diene which is excited to an electronic state more energetic than the first singlet state. This excited singlet either dissociates into a triplet-state diene and a triple-state ferrocene or undergoes intersystem-crossing to the second excited triplet state which dissociates into a triplet-state diene and a ground-state ferrocene. The triplet-state diene thus produced, either isomerizes or adds to a ground-state diene to form dimers.

Recent work by Hammond and coworkers has demonstrated the capacity of photosensitizers to promote the isomerization (1) and dimerization (2, 3) of several different compounds. In most cases the mechanism of sensitization involves transfer of energy and multiplicity from the first excited triplet (T_1) state of the photosensitizer to the ground (S_0) state of the acceptor. In some cases, for example the photoaddition of maleic acid to benzene, the photoreaction has been shown to proceed via the T_1 state of a complex (4). Cuprous chloride and rhodium chloride catalyze the photocyclization of 1,5-cycloctadiene by a mechanism which may involve a complex of the diene and metal salt (5, 6).

Electronic emission from complex molecules almost always occurs from the lowest excited state of a given multiplicity (7). The

accepted explanation for this phenomenon is that internal conversion is an extremely rapid process which very efficiently competes with radiative transitions and intersystem-crossing (7). The best documented exception to this rule is the fluorescence of azylene, which has been shown to be an $S_2 \rightarrow S_0$ process (8, 9). Ferrocene appears to be a second exception in that phosphorescence is observed when ferrocene is irradiated at 3240 Å, but not when it is irradiated at 4200-4400 Å (10).

Non-dissociative photochemical reactions are generally thought to arise from the lowest excited states for reasons analogous to those stated for radiative transitions. The general validity of this assumption is affirmed by such correlations as that of the $T_1 \leftarrow S_0$ energy of sensitizers with the photostationary states of photosensitized cis-trans isomerizations (1).

RESULTS

Irradiation of solutions of ferrocene and the piperylenes in the absence of air leads to isomerization of the piperylenes. Little or no isomerization occurs under the same conditions in the absence of ferrocene. The ferrocene-induced photoisomerization occurs in a variety of solvents including benzene, normal hexane, decalin and trans-1,2-dimethylcyclohexane. Extensive decomposition of ferrocene occurs in the presence of air, presumably caused by a photoxidation process. Ferrocene does not, however, decompose upon irradiation of evacuated ferrocene-piperlyene solutions.

Nature of the Exciting Radiation

Although the electronic spectrum of ferrocene extends into the visible region with a broad absorption band centered at 4400 Å (see Figure 1), only ultraviolet light effects the photoisomerization. No isomerization occurs when the exciting light is passed through a uranium glass filter, which absorbs part of the 3341 Å mercury emission line and all of the lines with wavelength less than 3341 Å (see Table 1 for the output of the lamps employed). Similarly, the isomerization is markedly slowed if a Pyrex emmersion well is used to house the mercury lamp. A 2 mm thickness of Pyrex absorbs approximately 50% of the light emitted at 3130 Å and 99% of the light emitted at 2800 Å (11). The radiation emitted by a lamp housed in a Pyrex emmersion well must penetrate approximately 3 mm of Pyrex. Clearly, light of

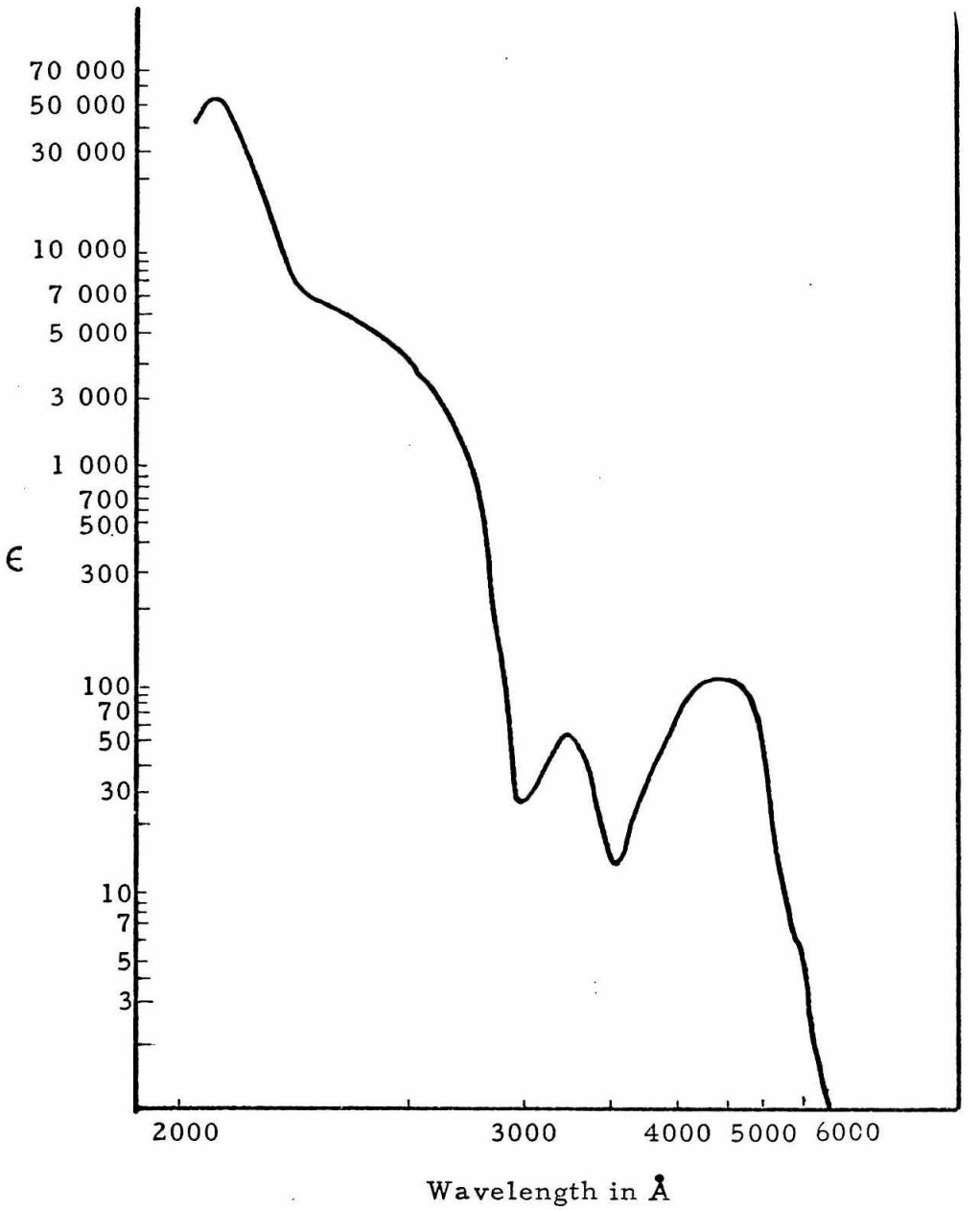

Figure 1. Absorption spectrum of ferrocene in isopentane (1).

Table 1

Ultraviolet Output of Mercury Lamps Used for Irradiations (12)

Wavelength Å	Radiated energy in watts
3660	25.6
3341	2.4
3130	13.6
3025	7.2
2967	4.3
2894	1.6
1804	2.4
2753	0.7
2700	1.0
2652	4.0
2571	1.5
2537 (reversed)	5.8
2482	2.3
2400	1.9
2380	2.3
2360	2.3
2320	1.5
2224	3.7

3130 Å wavelength promotes the photoisomerization while 3660 Å and 3341 Å radiation do not, (irradiation at 2537 Å also causes isomerization). Consequently, the exciting irradiation must be absorbed by that part of the spectrum which begins at the second absorption band (centered at 3240 Å) and extends to shorter wavelengths (see Figure 1).

Ferrocene-Piperylene Complex

The electronic spectra of mixtures of ferrocene and the piperylenes are not additive in the region below 3200 Å. We interpret this observation to indicate the formation of a complex between ferrocene and the piperylenes. In this regard, the spectrum of ferrocene has been found to be quite sensitive to impurities in the solvent, indicating that ferrocene probably complexes with many of these impurities.

The difference in absorbance between the λ_{max} of ferrocene at 3240 Å (the absorbance at the λ_{max} does not vary with added piperylene) and the λ_{min} at 3010 Å provides a convenient measure of the effect of added piperylene on the electronic spectrum of ferrocene. The change in the difference in absorbance between 3240 Å and 3010 Å is rapid at first upon addition of piperylene and then levels off to a more constant value (see Figure 2 and Table 2). The total piperylene concentration (both free and complexed) at the point where the curve of Figure 1 levels off is about 5×10^{-2} M. We shall define K, the formation constant for ferrocene-piperylene complex as in Equation 1.

$$K = \frac{[\text{complex}]}{[\text{ferrocene}][\text{piperylene}]} \qquad (1)$$

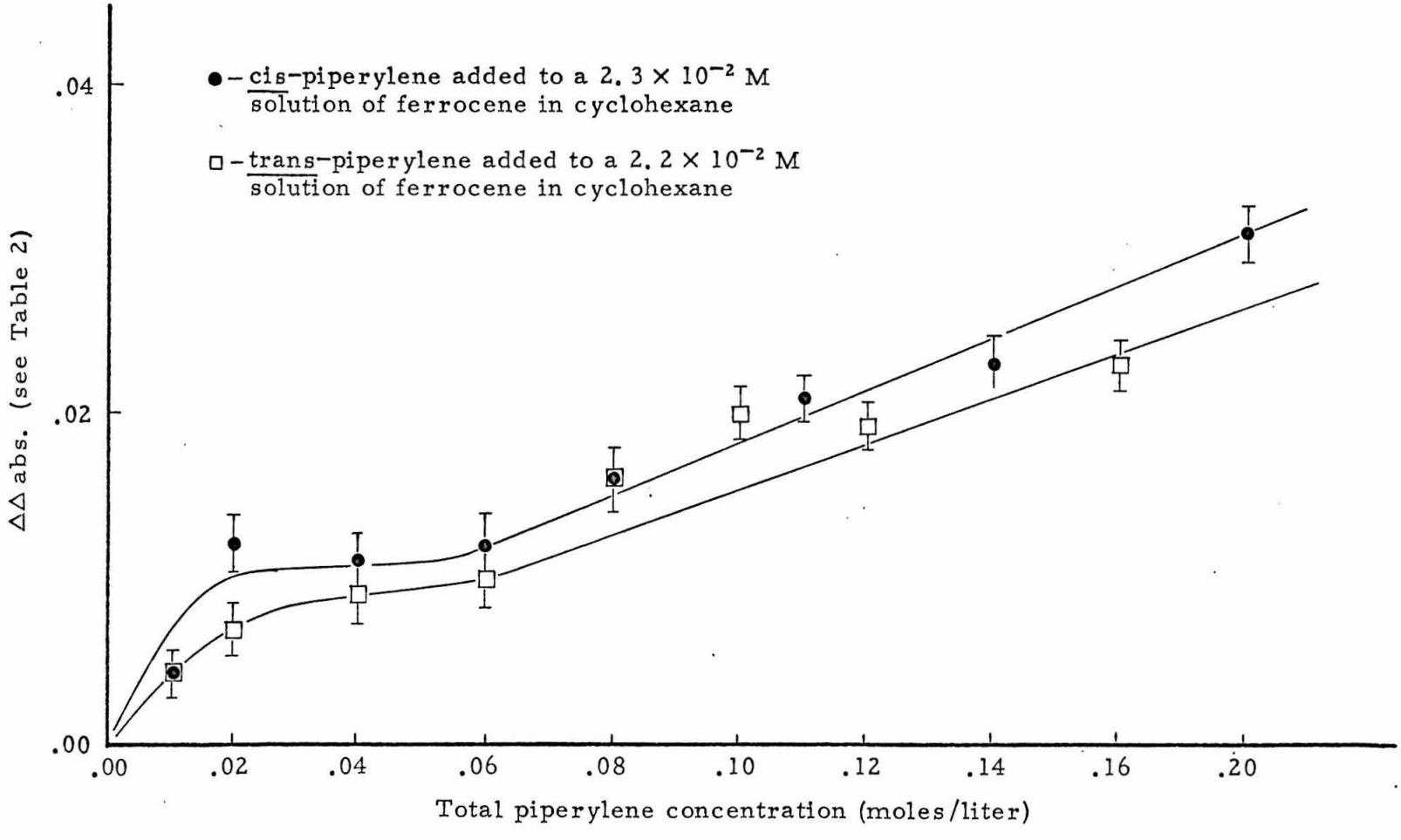

Figure 2. Change of ultraviolet spectrum of ferrocene upon addition of piperylene.

Table 2

Change of Ultraviolet Spectrum of Ferrocene
Upon Addition of Piperylene

Total ferrocene concentration	Total piperylene concentration		Δ Abs. *	ΔΔ Abs.**
2.3×10^{-2} cis	0	.774	.002	.000
"	1×10^{-2}	.770	.002	.004
"	2×10^{-2}	.762	.004	.012
"	4×10^{-2}	.763	.003	.011
"	6×10^{-2}	.768	.003	.012
"	8×10^{-2}	.758	.003	.016
"	11×10^{-2}	.753	.004	.021
"	14×10^{-2}	.751	.005	.023
"	18×10^{-2}	.743	.004	.031
"	60×10^{-2}	.674	.002	.100
2.1×10^{-2} trans	0	.691	.003	.000
"	1×10^{-2}	.687	.002	.004
"	2×10^{-2}	.684	.003	.007
"	4×10^{-2}	.682	.002	.009
"	6×10^{-2}	.681	.002	.010
"	8×10^{-2}	.678	.002	.013
"	10×10^{-2}	.671	.002	.020
"	12×10^{-2}	.672	.004	.019
"	16×10^{-2}	.670	.002	.021
"	30×10^{-2}	.647	.002	.044

Solvent: cyclohexane

* Difference in absorbance between λ_{max} (3240 Å) and λ_{min} (3010 Å) followed by average deviation. ** Difference between Δ abs. and Δ abs. for ferrocene alone.

Assume that the ratio of complex to free ferrocene is 10^{-2} at the point where the curve of Figure 1 levels off, that is when the total piperylene concentration is 5×10^{-2} M. The free piperylene concentration must, then, be about 3×10^{-2} M since the complex concentration is about 2×10^{-2} M. Substituting these values in Equation 1, we find $K \sim \frac{10}{3 \times 10^{-2}} \sim 300$.

Investigation of the change in the chemical shifts between the higher field peaks in the piperylene methyl doublets and TMS also produces evidence for association of ferrocene and piperylene (see Figure 3 and Table 3). However, the apparent formation constants, especially for the trans isomer, are smaller than those obtained from the ultraviolet measurements. If we take 1.1 M total ferrocene concentration as the point at which the ratio of free piperylene to complex is 10, then we obtain that $K \sim 100$ for cis-piperylene and $K \sim 25$ for trans-piperylene. We have more confidence in the values of K obtained from the ultraviolet measurements, because these measurements were made in dilute solution.

Due to the disparity between the various estimates of the formation constants for ferrocene-piperylene complex, we shall only assume that such a complex exists and that $K \geq 10$.

The new doublet that was previously reported to appear in the n. m. r. spectrum of ferrocene upon the addition of piperylene (13) was found to be spurious and could not be reproduced.

In the long wavelength portion of the electronic spectrum (wavelength greater than 3200 Å) the absorptions of ferrocene-piperylene

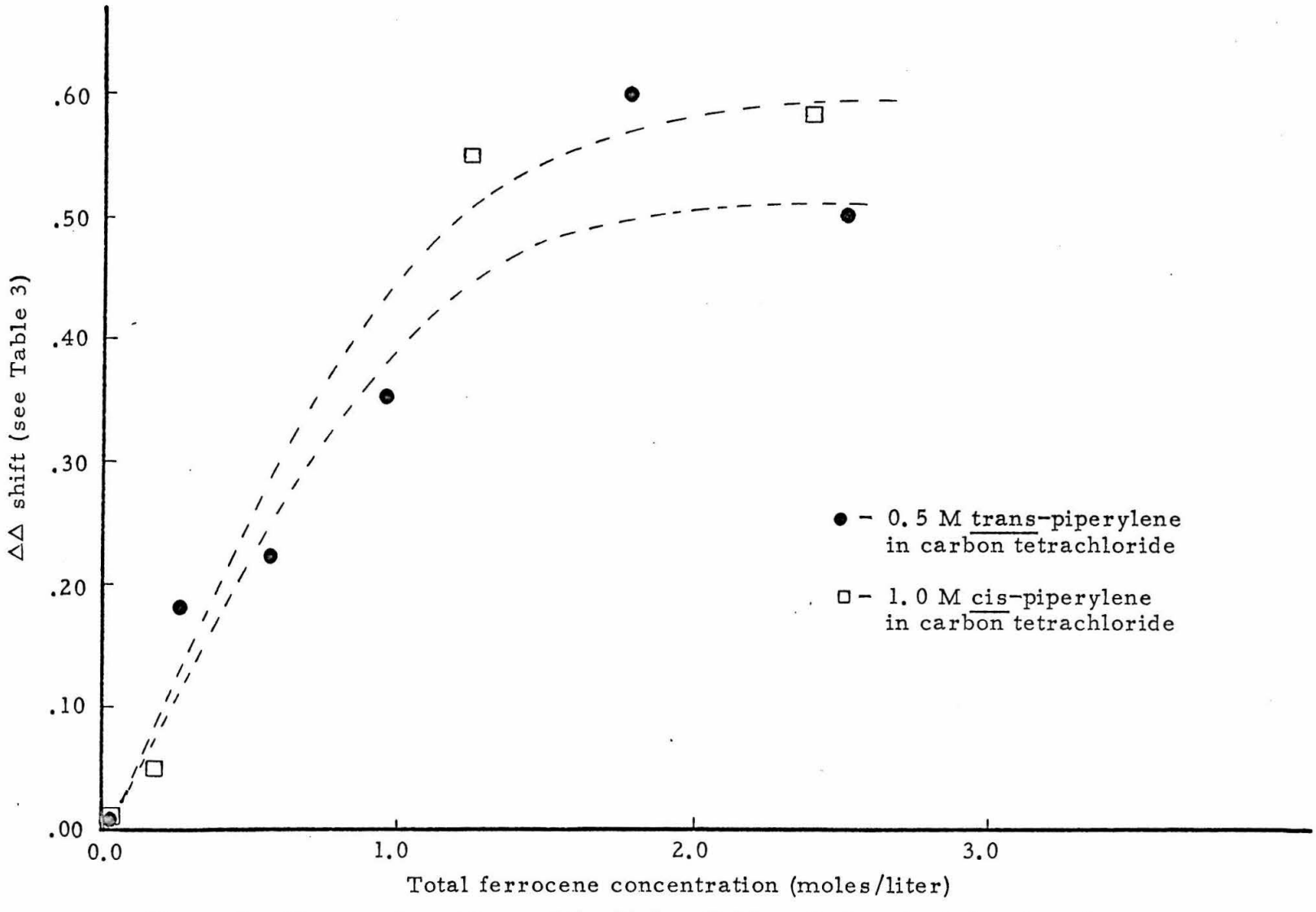

Figure 3. Change of positions of the higher field methyl peak of the piperylenes upon addition of ferrocene

Table 3

Change of Position of the Higher Field Methyl Peak of the Piperylenes Upon Addition of Ferrocene

concentration	concentration	Δ Shift *	ΔΔ Shift**
1.0 M cis	0	98.90 ± 0.03	0.00
"	0.16	98.85 ± 0.03	0.05
"	1.23	98.35 ± 0.03	0.55
"	2.4	98.32 ± 0.03	0.58
1.5 M trans	0	99.30 ± 0.03	0.00
"	0.25	99.12 ± 0.03	0.18
"	0.56	99.08 ± 0.03	0.22
"	0.96	98.95 ± 0.03	0.35
"	1.78	98.70 ± 0.03	0.60
"	2.53	98.80 ± 0.03	0.50

Solvent: carbon tetrachloride

* Difference between the position of the higher field peak of the methyl doublet of piperylene and TMS. ** Difference between Δ shift and Δ shift for piperylene with no ferrocene added.

mixtures are identical to that of ferrocene, indicating that the electronic spectra of the complexes are the same as that of ferrocene in that region. We, therefore, conclude that the electronic transitions of ferrocene that give rise to absorption bands at 4400 Å and 3240 Å are virtually unperturbed in the complex. We shall later find it helpful to assume that energies of the ground states and the excited singlet states involved in these transitions and the related energies of triplet states are the same for free ferrocene and its complex with piperylene.

Photostationary State

The measured photostationary state for the ferrocene induced photoisomerization of the piperylenes is 54.5% trans-piperylene (see Table 4). This photostationary state is the same as that measured for the corresponding benzophenone sensitized isomerization and reported for isomerizations induced by sensitizers which have a sufficiently high $T_1 \leftarrow S_0$ energy to sensitize both cis and trans-piperylene at a diffusion controlled rate (see Figure 4). Since, in such cases, triplet diene arises with equal ease from cis or trans isomer, the photostationary state depends only upon the decay ratio of the triplet state. We, therefore, interpret the observed photostationary state to affirm the intermediacy of triplet-state diene in the ferrocene-induced photisomerization. Furthermore, production of triplet-state diene must be equally facile from both cis and trans-diene.

Fry has observed that ferrocene functions quite well as a triplet quencher, even quenching triplets as low in energy as that of anthracene (43 kcal/mole) at a diffusion controlled rate (15). Saltiel and

Table 4

Photostationary States for Piperylene Isomerization

Sensitizer	Concentration of sensitizer	Concentration of piperylene	Photo-stationary state
Benzophenone*	0.05 M	0.05 M	54.5% trans
Ferrocene	0.05 M	0.05 M	54.5% trans
Benzophenone* (+ 0.05 M ferrocene as Quencher)	0.10 M	0.05 M	54.5% trans

* Uranium glass filter employed. No ferrocene-induced photoisomerization occurs when this filter is used (see text).

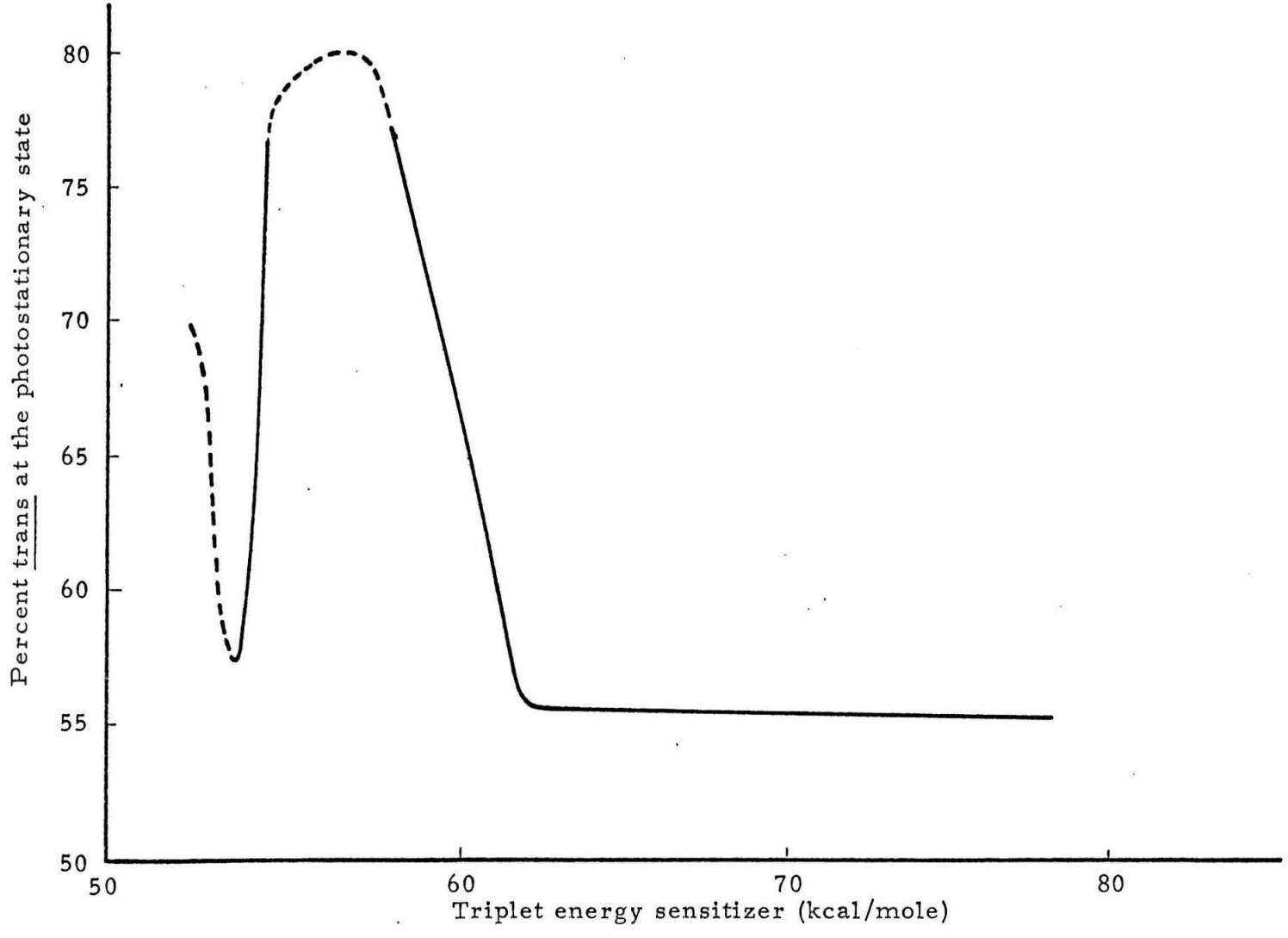

Figure 4. Photosensitized isomerization of the piperylenes

Hammond have reported that the photostationary state observed for the sensitized photoisomerization of the stilbenes depends upon the concentration of added quencher (16). To verify that the photostationary state observed for the ferrocene-induced photoisomerization is the result of the natural decay ratio of piperylene triplet and not the fortuitous combination of selective sensitization and selective quenching by ferrocene, the benzophenone sensitized photoisomerization was studied in the presence of ferrocene, added as a quencher. The irradiation conditions (light of 3660 Å wavelength was used) assured that benzophenone absorbed nearly all of the light and any light absorbed by ferrocene or ferrocene-piperylene complex should not result in isomerization. The presence of ferrocene did not affect the photostationary state of the benzophenone sensitized photoisomerization of the piperylenes (see Table 4). Thus, the observed photostationary state must be the result of the natural decay ratio of piperylene triplets.

Dimerizations

Irradiation of ferrocene solutions in neat piperylene or isoprene produces dimers of the dienes. Liu and Hammond have studied the photosensitized dimerization of isoprene in detail (2). They found that seven dimers result: three cyclobutanes, two cyclooctadienes, and two cyclohexanes. They explained their observation that the product distribution changed as a function of the $T_1 \leftarrow S_0$ energy of the sensitizers used (see Figure 5) in terms of differing rates of energy transfer from sensitizer to cisoid and transoid-isoprene. High energy sensitizers, those that can transfer energy to either conformation with

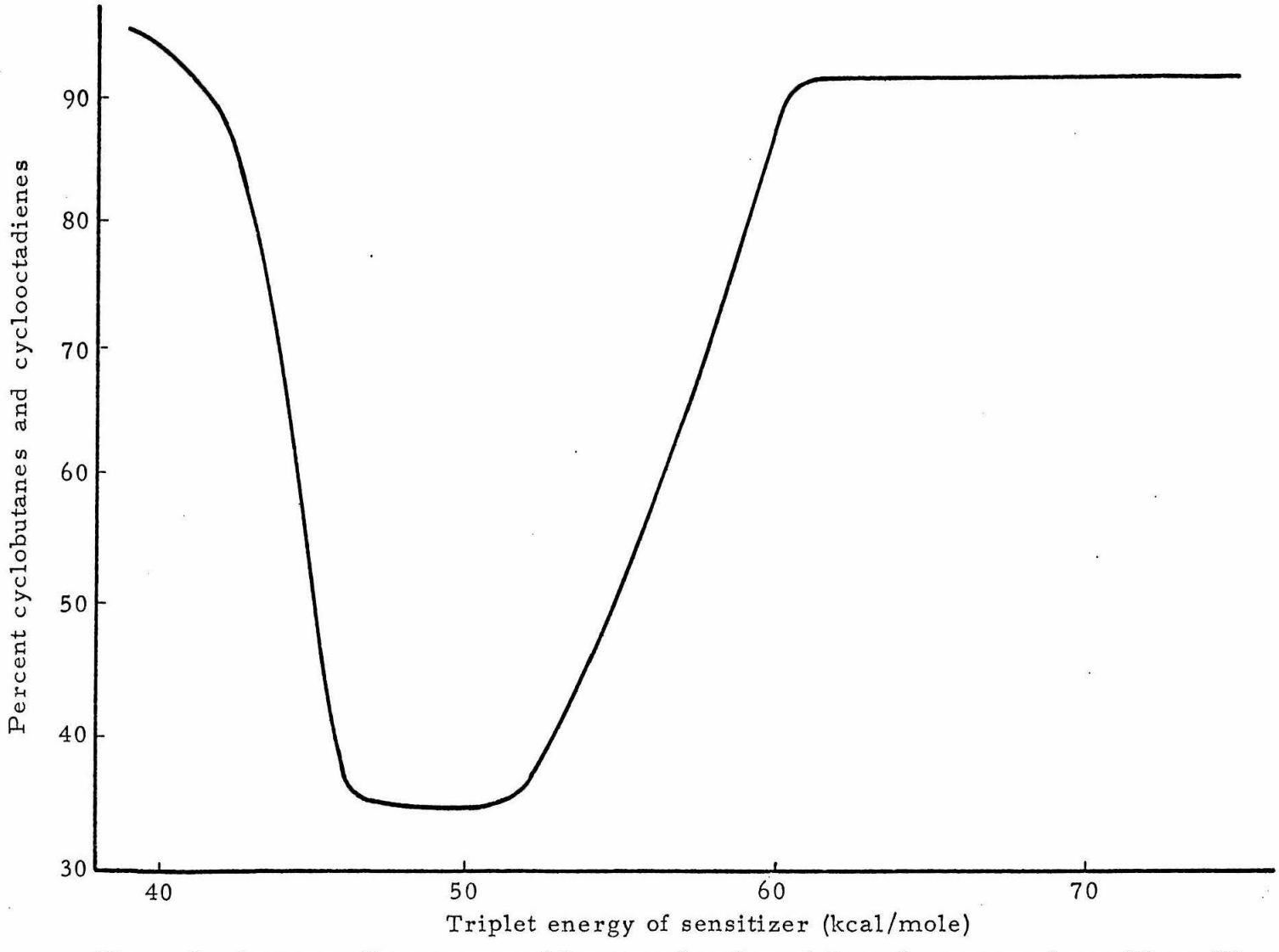

Figure 5. Isoprene dimer composition as a function of $T_1 \leftarrow S_0$ energy of sensitizer (2).

equal probability, produce a mixture of dimers that contain 92% cyclobutanes and cyclooctadienes. Similarly, the ferrocene-induced photodimerization of isoprene produces 92% cyclobutanes and cycloctadienes. The observation that the isoprene dimer distribution is the same for photodimerization induced either by ferrocene or by high energy sensitized suggests that the ferrocene-induced process also involves production of cisoid and transoid-isoprene triplets with equal probability. Thus, the lack of selectivity in ferrocene-photoinduced isoprene triplet production parallels the lack of selectivity in ferrocene-photoinduced piperylene triplet formation mentioned above.

Quantum Yields

The quantum yields for the ferrocene-induced photoisomerization of both isomers of piperylene (see Table 5) indicate that the efficiency of the isomerization is of the order of a few percent. The photoisomerization was monitored at several time intervals corresponding to from 0.5 to 5% conversion as a precaution against possible complications due to secondary reactions. No such complications occurred. The extent of isomerization varied linearly with the irradiation time (see Figures 6 and 7). The quantum yields listed in Table 5 were calculated from the slopes of the lines in Figures 6 and 7. These quantum yields are expressed in terms of the number of triplet-state diene molecules produced, rather than the number of diene molecules isomerized. The good agreement between the quantum yields for triplet production from both isomers at similar concentrations again indicates that production of triplet-state diene molecules is equally efficient

Table 5

Quantum Yields for the Production of Triplet-State Piperylene

Concentration of piperylene (moles/l)	Concentration of ferrocene (moles/l)	Quantum yield (whole solution)	Quantum[a] yield corrected	Quantum[b] yield
0.010 *trans*	0.162	0.0033	0.0033	0.048
0.010 *cis*	0.144	0.0034	0.0032	0.049
0.024 *trans*	0.162	0.0041	0.0041	0.025
0.024 *cis*	0.144	0.0059	0.0053	0.033
0.061 *trans*	0.162	0.011	0.011	0.026
0.061 *cis*	0.144	0.012	0.011	0.027
0.101 *trans*	0.162	0.013	0.013	0.020
0.101 *cis*	0.144	0.016	0.014	0.021

[a] Correction assumes the same amount of complex in the *cis* and *trans* experiments run at similar piperylene concentration and corrects for internal filtering by ferrocene.

[b] For complex assuming complex has the same extraction coefficient as ferrocene at 3130 Å and all the piperylene is complexed.

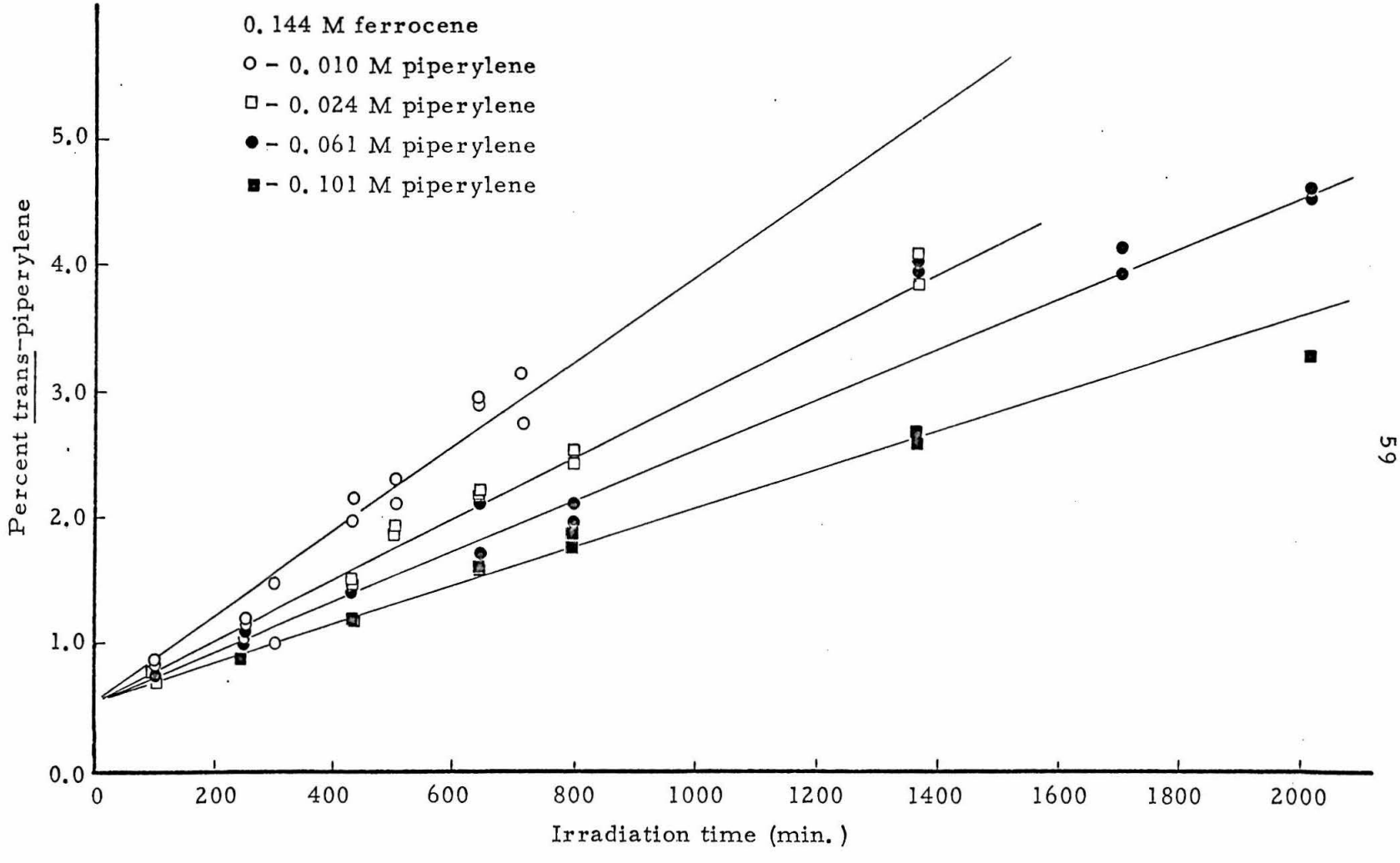

Figure 6. Ferrocene-induced photoisomerization of the cis-piperylene

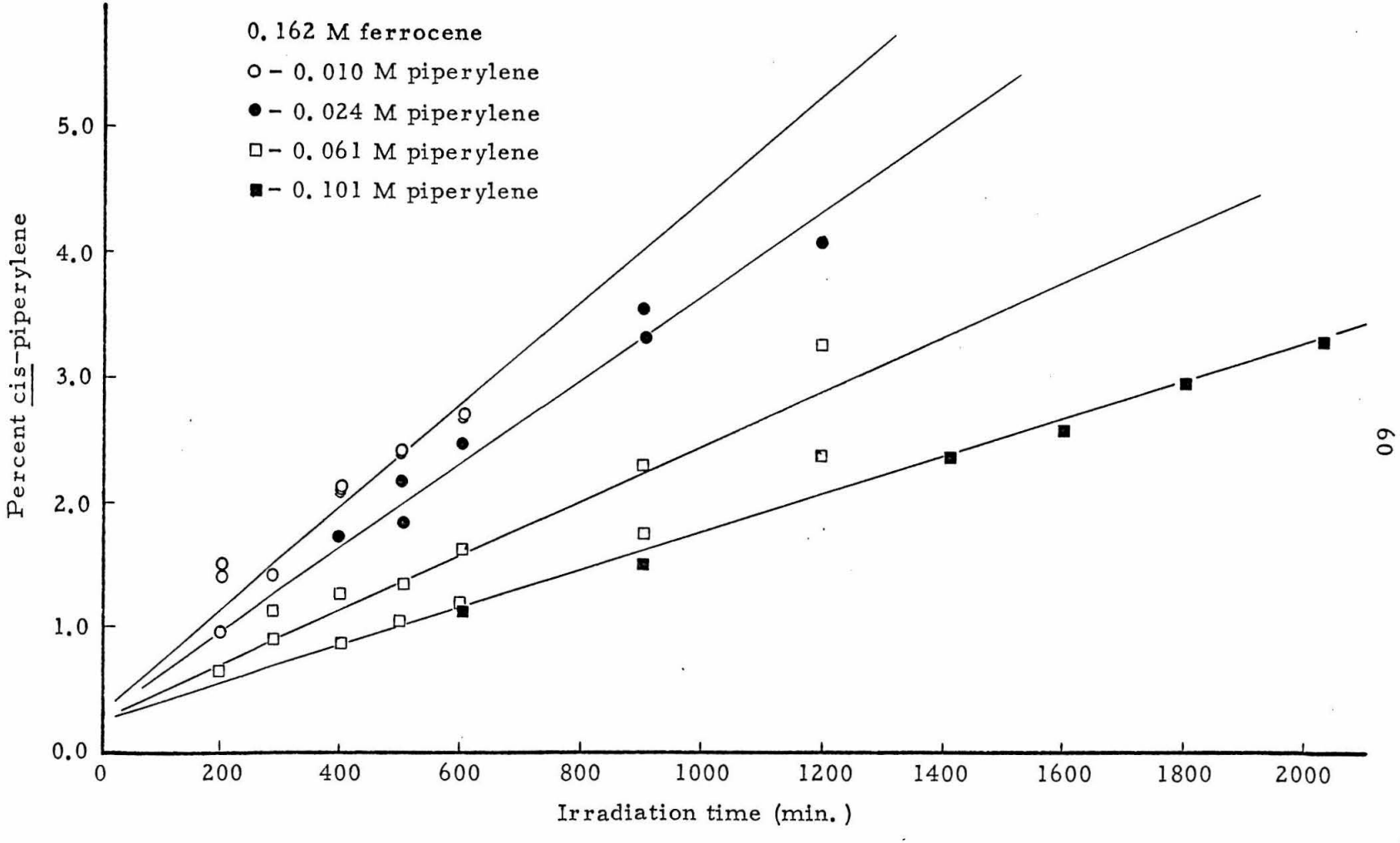

Figure 7. Ferrocene-induced photoisomerization of trans-piperylene

from both isomers. As is evident from Tables 5 and 6, the quantum yields are dependent upon the concentrations of ferrocene and piperylene.

Table 6

Relative Quantum Yields of Ferrocene-Induced Photoisomerization of trans-Piperylene in Benzene Solution

Total ferrocene concentration	Total trans-piperylene concentration	Relative quantum yields
0.05 M	0.01 M	1.0
0.05 M	0.10 M	4.2
0.05 M	0.5 M	4.4

DISCUSSION

The photostationary observed state for the ferrocene-induced photoisomerization of the piperylenes, the product distribution obtained from the ferrocene-induced photodimerization of isoprene are both identical to the observed photostationary states and product distributions for the analogous reactions when high energy sensitizers, such as benzophenone, are employed (1, 2). Since the intermediacy of triplet-state diene has been established for the photosensitized reactions (1), we, likewise, presume the intermediacy of triplet-state diene in the ferrocene-induced photoreactions.

Several possible mechanisms for the ferrocene-induced photoisomerization of the piperylenes which involve triplet-state diene as an intermediate are enumerated below:

1. Ferrocene acts as a photosensitizer in a manner analogous to that of benzophenone.
2. The complexes formed between ferrocene and the piperylenes act as photosensitizers in a manner analogous to that of benzophenone.
3. The iron atom in ferrocene induces direct $T_1 \leftarrow S_0$ transition in the piperylenes.
4. The complex is excited to an S_2 state,* which crosses

* Here and throughout this thesis, the S_2 state of ferrocene and ferrocene-piperylene complex is used to denote the singlet state formed when ferrocene or complex is excited by the light of wavelength centered at 3240 Å. S_1 will be used to refer to the singlet state formed by irradiation with light of wavelength centered at 4400 Å. T_1 and T_2 represent the triplet states which correspond to S_1 and S_2.

over to a triplet state before it dissociates into a T_1 diene and an S_0 ferrocene.

5. The complex is excited to an S_2 state which dissociates into a T_1 diene and a T_1 ferrocene.

Once the T_1 diene has been formed, the isomerization proceeds in the manner already described for photosensitized isomerizations (1). We shall discuss each mechanism individually for the purpose of evaluating it with respect to the observed experimental results.

Ferrocene as a Photosensitizer

$$\text{ferrocene} \xrightarrow{h\nu} \text{ferrocene}^{S_1 \text{ or } S_2} \tag{2}$$

$$\text{ferrocene}^{S_1 \text{ or } S_2} \longrightarrow \text{ferrocene}^{T_1 \text{ or } T_2} \tag{3}$$

$$\text{ferrocene}^{T_1 \text{ or } T_2} + \text{piperylene}^{S_0} \longrightarrow \text{piperylene}^{T_1} + \text{ferrocene}^{S_0} \tag{4}$$

If ferrocene acts as a photosensitizer, it must undergo excitation to an excited state, cross over to a triplet state, and, subsequently, transfer both its energy and multiplicity to ground-state diene encountered in solution. Among the attributes of a good triplet sensitizer are a triplet state that is both sufficiently long-lived to ensure a reasonable number of encounters with acceptor molecules and sufficiently energetic to allow exothermic energy transfer to the acceptor.

The first absorption band in the electronic spectrum of ferrocene is quite broad and centered at 4400 Å (65 kcal/mole) (see Figure 1). Since the $S_1 \leftarrow S_0$ energy is significantly greater than the $T_1 \leftarrow S_0$ for most compounds, the $T_1 \leftarrow S_0$ energy of ferrocene should be signi-

cantly less than 65 kcal/mole. The observation that ferrocene is an exceedingly effective triplet quencher, quenching triplets as low in energy as that of anthracene ($T_1 \leftarrow S_0$ energy = 43 kcal/mole (17)) at a diffusion-controlled rate (15) (see above) indicates that the $T_1 \leftarrow S_0$ energy for ferrocene must be less than 40 kcal/mole since diffusion-controlled energy transfer is observed when such transfer is exothermic by at least 3 kcal/mole (18).

We have considered the possibility that the marked quenching ability of ferrocene may be due to a heavy atom effect. Such an effect would markedly reduce the lifetime of excited triplet states in close proximity to ferrocene molecules. Studies of triplet quenching by various iron chelates indicate that chelates with receptive low-lying π-orbitals quench at nearly a diffusion-controlled rate, whereas ferric chloride, which lacks π-orbital does not quench triplets (19). Furthermore, studies of naphthalene phosphorescence in rigid glasses containing heavy atoms (chlorine, bromine, iodine) indicated that the greatest increase in the rate constant for quenching of phosphorescence was only a factor of two for a glass containing ethanol, methanol, and n-propyl iodide in ratio 4:1:1 (20). Since ferric chloride and these glasses exhibit little or no heavy atom quenching effects, such effects must not be largely responsible for the observed extremely efficient triplet quenching by ferrocene.

If Kasha's estimate of 10^{13} sec.$^{-1}$ for the rate constant for internal conversion (7) be applicable to ferrocene, the only triplet state of ferrocene which could exist long enough to transfer its energy must be the T_1 state. Although, sensitization of the piperylenes by sensi-

tizers with $T_1 \leftarrow S_0$ energies considerably below those of the piperylenes has been reported (1), the resulting photostationary states vary with the $T_1 \leftarrow S_0$ energy of the sensitizer used, whereas high energy sensitizers all produce the same photostationary state (see Figure 4) (1). Photostationary states for piperylene isomerization have not been reported for sensitizers with $T_1 \leftarrow S_0$ as low as 40 kcal/mole. Nevertheless, the likelihood that the photostationary states produced by such low energy sensitizers would be exactly the same as that produced by high energy sensitizers is small. The observation that light of wavelength 3341 Å or larger does not effect ferrocene-induced photoisomerization of the piperylenes indicates that excitation of ferrocene to its S_1 state does not produce any isomerization of the piperylenes.

In the case of ferrocene, Kasha's estimated value for the rate of internal conversion is probably incorrect. Scott and Becker (10) have reported that ferrocene probably phosphoresces from the T_2 state, with a lifetime of 2 seconds, thereby, making ferrocene, along with azulene the only known compounds which emit light from excited states other than the lowest excited state of each multiplicity. Scott and Becker did not see a triplet of lower energy than that at 54 kcal/mole. They, however, acknowledged the possibility that the triplet that phosphoresced was the lowest triplet, although this triplet must be inaccessible from the first singlet. The observation that ferrocene efficiently quenches anthrocene triplets (15) (see above) strongly suggests that ferrocene does possess a triplet state of significantly lower energy than 54 kcal/mole, which supports the interpretation that the phosphorescing species is, in fact, the second triplet state.

Since the T_2 state of ferrocene is sufficiently long-lived, we must consider the possibility of energy transfer from this excited state to the piperylenes. Scott and Becker (10) assigned the 5280 Å (54 kcal/mole) weak shoulder of the ferrocene absorption spectrum to a singlet-triplet transition, presumably $T_2 \leftarrow S_0$. A sensitizer with a triplet energy of 54 kcal/mole cannot be considered a high energy sensitizer for piperylene isomerization (1). Nevertheless, the plot of photostationary state of piperylene versus $T_1 \leftarrow S_0$ energy of sensitizers (1), reproduced here as Figure 4, exhibits a minimum which corresponds to a sensitizer $T_1 \leftarrow S_0$ energy of 54 kcal/mole and a photostationary state similar to those produced by high energy sensitizers. However, a sensitizer with a triplet energy of 54 kcal/mole should not yield the mixture of isoprene dimers characteristic of high-energy sensitizers (2) (see Figure 5).

We feel that the observed photostationary states and dimer distribution present a compelling argument against sensitization of the piperylenes by either the T_1 or T_2 state of ferrocene.

Ferrocene-Piperylene Complex as a Sensitizer

$$\text{ferrocene} + \text{piperylene} \rightleftarrows \text{complex} \tag{5}$$

$$\text{complex}^{S_0} \xrightarrow{h\nu} \text{complex}^{S_1 \text{ or } S_2} \tag{6}$$

$$\text{complex}^{S_1 \text{ or } S_2} \longrightarrow \text{complex}^{T_1 \text{ or } T_2} \tag{7}$$

$$\text{piperylene}^{S_0} + \text{complex}^{T_1 \text{ or } T_2} \longrightarrow \text{piperylene}^{T_1} + \text{complex}^{S_0} \tag{8}$$

The observation that no significant deviation from Beer's Law

occurs for the first to absorption bands of the electronic spectra of mixtures of ferrocene and the piperylenes suggest that the lower excited states of the complex (S_1, S_2, T_1, and T_2) are isoenergetic with the analogous excited states of ferrocene. Under these circumstances, the arguments which make energy transfer from the triplet states of ferrocene untenable as mechanistic possibilities apply to energy transfer from the triplet states of the complex with equal cogency.

Ferrocene-Induced Direct $T_1 \leftarrow S_0$ Absorption of the Piperylenes

$$\text{piperylene} \xrightarrow[\text{ferrocene}]{h\nu} \text{piperylene}^{T_1} \qquad (9)$$

The $T_1 \leftarrow S_0$ transitions of cis and trans-piperylene require 56.9 and 58.8 kcal/mole respectively (21). Their $T_1 \leftarrow S_0$ absorptions should occur at 5030 Å and 4860 Å. The observation that only light of shorter wavelength than 3341 Å effects the ferrocene-induced photoisomerization of the piperylenes precludes any mechanistic possibilities involving direct $T_1 \leftarrow S_0$ absorption by the piperylenes.

Dissociation by Triplet-State Complex

$$\text{ferrocene} + \text{piperylene} \rightleftarrows \text{complex} \qquad (5)$$

$$\text{complex} \xrightarrow{h\nu} \text{complex}^{S_2} \qquad (10)$$

$$\text{complex}^{S_2} \longrightarrow \text{complex}^{T_2} \qquad (11)$$

$$\text{complex}^{T_2} \longrightarrow \text{piperylene}^{T_1} + \text{ferrocene} \qquad (12)$$

As mentioned above, the virtual identity of the long-wavelength part of the spectra of mixed solutions of ferrocene and the piperylenes

implies that the lower excited states (S_1, S_2, T_1, T_2) of ferrocene and complex are similar. Irradiation of the longest wavelength band of the mixed ferrocene-piperylene solutions produces no isomerization of the piperylenes; therefore, the first excited singlet state of the complex must not be an intermediate in the isomerization. If the photoisomerization proceeds via an excited state of the complex, the initial excited state must be the second or higher excited singlet state. If the S_2 complex behaves similarly to S_2 ferrocene, an appreciable amount of S_2 complex can cross over to the triplet manifold to produce the T_2 state of the complex. The T_2 complex might then dissociate into T_1 piperylene and ground-state ferrocene (reaction 12). The second, rather than the first, excited triplet of the complex must be the state that dissociates. The first excited triplet must have a $T_1 \leftarrow S_0$ energy similar to that of ferrocene (40 kcal/mole, see above). A dissociation of T_1 complex into T_1 piperylene should be highly endothermic; therefore, such a process should not successfully compete with other possible processes such as dissociation to a T_1 ferrocene and a ground-state piperylene (Reaction 13), or intersystem-crossing to ground-state complex (Reaction 14). Because the $T_2 \leftarrow S_0$ (54 kcal/mole) of

$$\text{complex}^{T_2} \longrightarrow \text{ferrocene}^{T_1} + \text{piperylene}^{S_0} \qquad (13)$$

$$\text{complex}^{T_2} \longrightarrow \text{complex}^{S_0} \qquad (14)$$

ferrocene, and therefore of complex, is less than the $T_1 \leftarrow S_0$ energy of the piperylenes (56.9 and 58.8 kcal/mole (21) for trans and cis respectively) the dissociation of T_2 complex (Reaction 12) should be endothermic by about 5 kcal/mole. The triplet energies referred to

above are those of the spectroscopic triplet-states which, as a result of the Franck-Condon Principle, have the same molecular geometry as do the ground states. Because the geometry corresponding to the lowest energy conformation of an excited state need not be the same as the geometry of the ground state, the conformation of the vibrationally relaxed triplet state might be significantly different from that of the spectroscopic triplet. Consequently, the energy of the vibrationally relaxed triplet might be somewhat less than that measured by absorption spectra. If the vibrational excitation of the spectroscopic T_1 piperylene be greater than that of the spectroscopic T_2 complex, the dissociation of T_2 complex may be less endothermic than was estimated above, or it may even be exothermic. Since the rings of ferrocene are presumably rigid, any vibrational relaxation of the ferrocene-piperylene complex should be manifest either as a twisting of one of the piperylene double bonds in a manner similar to that proposed by Mulliken for the vibrationally relaxed electronic excited states of butadiene (22) or of some change in the relative positions of ferrocene and piperylene. The excited complex may not be able to accommodate much twisting of the piperylene double bonds without dissociating. Therefore, the double bonds of the vibrationally relaxed free piperylene triplets probably are more twisted than the corresponding double bonds of piperylene in the vibrationally relaxed ferrocene-piperylene complex. Thus, the amount of vibrational excitation in the spectroscopic T_2 complex may be sufficiently less than that of the spectroscopic piperylene triplets to allow the dissociation of T_2 complex to T_1 piperylene and S_0 ferrocene (Reaction 12) to be exothermic.

If the dissociation of T_2 complex to S_0 ferrocene and T_1 piperylene (Reaction 12) be endothermic, the T_2 states of ferrocene-cis-piperylene complex and the ferrocene-trans-piperylene complex should not dissociate at the same rate unless the activation energies for the two dissociations be the same. The two dissociations will probably be endothermic by different amounts since the double bonds of piperylene in the vibrationally relaxed T_2 complex are probably not as twisted as those in a free piperylene triplet. Consequently, unlike free piperylene triplet, the T_2 complexes of cis and trans-piperylene with ferrocene probably maintain their isomeric integrity. Thus, there is no reason to expect the activation energies for the dissociations of the cis and trans-piperylene-ferrocene complexes to be equivalent.

If the rates of dissociation for the ferrocene complexes with cis and trans-piperylene differ, the photostationary state should not be the same as that produced by energy transfer from high-energy sensitizers; rather, the photostationary state should reflect the selectivity of the dissociation reactions. The above argument will obtain unless a selectivity for complex formation should exist which would exactly compensate for the selectivity in the dissociation of the excited complex. An analogous compensating selectivity in the formation of complex between the cisoid and transoid forms of isoprene and ferrocene would have to be invoked to explain the observation that the ferrocene-induced dimerization of isoprene produces the same mixture of dimers as does energy transfer from high-energy sensitizers. The possibility that exactly compensating selectivities of complex formation and T_2 complex dissociation exists for both cases is small.

One should note that if T_2 complex molecules dissociate to form T_1 diene and S_0 ferrocene (Reaction 12) to the exclusion of decay to ground state complex (Reaction 14) and dissociation to form T_1 ferrocene and S_0 piperylene (Reaction 13), no compensating selectivities of complex formation and T_2 complex dissociation to form T_1 piperylene need be invoked. However, if the dissociation of T_2 complex to form T_1 diene be endothermic, one would expect Reactions 13 and 14 to compete with dissociation to form T_1 diene. Such competition precludes the possibility that all T_2 complex molecules dissociate to form T_1 diene and S_0 ferrocene.

Thus, an isomerization mechanism which involves endithermic dissociation by either T_1 or T_2 complex is difficult to reconcile with the data, although an exothermic dissociation remains a possibility.

Dissociation by Singlet-State Complex

$$\text{ferrocene} + \text{piperylene} \rightleftarrows \text{complex} \tag{5}$$

$$\text{complex}^{S_0} \xrightarrow{h\nu} \text{complex}^{S_2} \tag{10}$$

$$\text{complex}^{S_2} \longrightarrow \text{piperylene}^{T_1} + \text{ferrocene}^{T_1} \tag{15}$$

We have already established that an $S_2 \leftarrow S_0$ transition must occur if absorption by complex be the primary photochemical process. The longest wavelength light that has been used to effect the ferrocene-induced isomerization is 3130 Å (92 kcal/mole). $T_1 \leftarrow S_0$ of ferrocene must be less than 40 kcal/mole (see above) and indeed there is no evidence which precludes the possibility that the $T_1 \leftarrow S_0$ energy of ferrocene may be much lower than 40 kcal/mole. Dissociation of S_2

complex into spectroscopic T_1 ferrocene and T_1 piperylene would be an exothermic process if the $T_1 \leftarrow S_0$ energy of ferrocene be about 32 kcal/mole or less. Such a dissociation process would account for the nonselective production of triplets from both isomers of piperylene if both isomers complex equally well with ferrocene. To apply this mechanism to the ferrocene-induced dimerization of isoprene, we must likewise, assume that the two different conformations of isoprene complex equally well with ferrocene. These assumptions, which amount to assuming that ferrocene complexes nonspecifically with these conjugated dienes, are much more reasonable than the variations of complex specificities necessary to rationalize the endothermic dissociation of T_2 (see above).

The dissociation of singlet-state complex into triplet-state molecules conserves electron spin and is simply the microscopic reverse of the well-documented triplet-triplet annihilation process (24, 25).

The lifetime of the S_2 complex may be quite short, possibly of the order of a few molecular vibrations, since the reaction is unimolecular and exothermic.

Quantum Yields

The quantum yields for production of piperylene from both *cis* and *trans*-piperylene are identical (see Table 5). Thus, the quantum yields predict that the photostationary state should depend only upon the decay ratio from triplet state piperylene, in good agreement with the observed photostationary state.

Since the formation constants are large for both *cis* and *trans*-

isomers of piperylene, both isomers must exist mostly in the form of complex in the quantum yield runs, especially those run at low piperylene concentration. The identity of the quantum yields at each concentration implies that the probability of S_2 complex dissociating into ferrocene and piperylene triplets (Reaction 14) is the same for complexes both of cis and trans-piperylene.

The quantum yield data (Table 5) indicate that the quantum yields decrease with increasing complex concentrations in the presence of excess ferrocene. The relative quantum yields of Table 6 indicate that the quantum yields increase with increasing piperylene concentration in the presence of excess piperylene. One possible explanation for this observation is that a piperylene molecule may complex with more than one ferrocene molecule in the presence of excess ferrocene and that a ferrocene molecule may complex with more than one piperylene molecule in the presence of excess piperylene. These complexes may undergo photolysis with quantum yields different from each other and different from the quantum yield for the 1:1 complex. Since the quantum yields were calculated under the assumption that only 1:1 complexes exist, the existence of these other complexes may explain the concentration dependence of the quantum yields.

EXPERIMENTAL

Materials

Ferrocene -- Ferrocene was obtained commercially from K and K Chemical Company and recrystallized from n-heptane, m. p. 172°.

trans-Piperylene -- trans-Piperylene was prepared by preparative vapour phase chromatography from commercially available technical grade piperylene. Two passes through 12 foot β, β, β-oxytripropionitrile columns at room temperature afforded 99. 7% trans-piperylene. After distillation, the pure trans isomer was stored in sealed evacuated ampules in a food freezer until used.

cis-Piperylene -- The cis isomer was obtained by two different methods: 1) by preparative vapour phase chromatography using 12 foot β, β, β-oxytripropionitrile at room temperature of a mixture of cis-piperylene and cyclopentene obtained from A. A. Lamola; 2) commercially from Columbia Organic Chemicals. The first method afforded virtually 100% cis-piperylene, whereas the commercial material afforded 98. 5% cis-piperylene, 0. 5% trans-piperylene and 1% cyclopentene.

Isoprene -- Isoprene was obtained commercially and distilled before use.

Solvents -- The solvents used for the photolyses had to be free of impurities which might complex with ferrocene or interfere with the vapour phase chromatographic analyses employed.

Benzene: 1) Reagent grade benzene was stirred with sulfuric

acid for approximately one week, or until the acid (which was changed daily) was no longer discolored by the benzene. The benzene was refluxed over phosphorous pentoxide overnight and then distilled. The first half of the distillate was discarded and the remainder of the distillate was used. 2) Phillips Research Grade (99. 9%) benzene was tested by vapour phase chromatography and some lots proved to be acceptable. Benzene obtained commercially from James A. Hinton (99. 99%) was similarly tested and also proved adequate.

Hexane: Phillips Pure Grade was used without further purification.

Decalin: Reagent grade decalin was stirred over sulfuric acid until the acid was no longer discolored by further stirring. The decalin was then distilled. The various fractions were tested by vapour phase chromatography. The higher boiling fractions proved to be acceptable.

trans-1, 2-Dimethylcyclohexane: Phillips Research Grade (99. 9%) trans-1, 2-dimethylcyclohexane was stirred over sulfuric acid until the acid was no longer discolored upon further stirring. The hydrocarbon was then distilled utilizing a spinning band column and stored under a nitrogen atmosphere in a refrigerator.

Cyclohexane: Matheson, Coleman and Bell, spectro grade was used without further purification.

Analyses

Product analyses for the isomerization of the piperylenes were performed by vapour phase chromatography using a 50 foot by $\frac{1}{8}$ inch, 25% β, β-oxydipropionitrile column at 20-45°. Analyses of the dimers

of isoprene were performed using a 6 foot by $\frac{1}{4}$ inch, 20% apiezon L column at 100°. Peak areas were measured either with a planimeter or by cutting out and weighing the peaks.

Irradiations

Irradiations were carried out in sealed evacuated test tubes. Light was provided by a 450 watt Hanovia medium pressure mercury lamp housed in a quartz immersion well. The well was placed in the center of a circular rotating test tube holder containing the experimental samples.

Quantum Yields

Sealed evacuated tubes containing the experimental samples were placed in a circular rotating stage designed to admit light only through carefully machined windows of equal dimensions. The windows were so shaped that no incident light could fall on the edges or bottoms of the tubes, thus eliminating errors caused by small variations of the dimensions of the tubes. Each tube contained exactly 3.0 ml. of sample. A Hanovia 450 watt medium pressure mercury lamp housed in a specially designed quartz immersion well with two concentric reservoirs for filter solutions, each 1 cm. thick, provided the radiation. To isolate the 3130 Å mercury emission line, a 1 cm. thickness of a filter solution prepared by dissolving 10 g. sodium carbonate and 0.5 g. sodium dichromate in enough water to make 1 liter was used. From the spectrum of the filter solution and the output characteristics of the lamp, supplied by the manufacturer , we determined that ultraviolet light other than that at 3130 Å was limited to 3.4% of the light

transmitted by the filter solution. Most of this 3.4% was at 3025 Å (see Table 7). All reaction tubes were sufficiently concentrated to absorb at least 99.9% of the light at 3130 Å.

The benzophenone (0.06 molar) photosensitized isomerization of the appropriate isomer of piperylene (0.05 molar) provided a convenient standard photolysis for actinometry. The sum of the quantum yields for benzophenone-sensitized photoisomerization of the two isomers of piperylene is 1.0 (26), indicating that the quantum yield for the production of triplet piperylene is one for both isomers.

Spectra

Ultraviolet and visible spectra were measured with Carey 14, Carey 11 and Beckman DU spectrophotometers. Nuclear magnetic resonance spectra were measured with Varian Model A-60 and A-60A spectrometers.

The ultraviolet spectra which provided the data for Table 2 and Figure 2 were measured at least five times each with a Carey 14 recording spectrophotometer. Solutions were made by adding a constant amount (with a syringe fitted with a spring-loaded constant measuring device) of a stock ferrocene solution to a volumetric flask, adding the appropriate amount of piperylene and diluting to volume.

The n.m.r. spectra which provided the data for Table 3 and Figure 3 were measured on Varian A-60A spectrometer, using a 100 cycle sweep width. Each δ was measured at least four times. The solutions were made up to be ~ 0.5 M and ~ 1.0 M for trans and cis-piperylene, respectively. Ferrocene was gradually added to the

Table 7

Distribution of the Ultraviolet Radiation

Used for Quantum Yields at 3130 Å

Wavelength	Rated power in watts	% Transmittance of filter solution	Transmitted power in watts	% of total
2537	5.8	6×10^{-8}	0.000	0
2967	4.3	0.006	0.003	0.2
3025	7.2	0.5	0.036	3.0
3130	13.2	8.9	1.18	96.6
3341	2.4	0.01	0.002	0.2
3360	25.6	$< 10^{-15}$	0.000	0

solutions. The relative amount of ferrocene was determined by integrating the ferrocene peak and the methyl peaks of the piperylenes.

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"Only in obedience I send you some of my paradoxes."

John Donne

PROPOSITIONS

Proposition I

The intensity of the Mössbauer effect is related to f, the fraction of resonance scattering events which occur without nuclear recoil of the absorber (1). The fraction of recoiless transitions, f, is, in turn, related to $\langle X^2 \rangle$, the mean square vibrational amplitude in the direction of the incident γ rays of the Mössbauer nucleus by equation 1, where λ is the wavelength of the scattered radiations (2). Because of this

$$f = \exp\left[-\left(\frac{4\pi^2 \langle X^2 \rangle}{\lambda^2}\right)\right] \qquad (1)$$

dependence of f upon $\langle X^2 \rangle$, an anisotropic Mössbauer effect should be observable if the structure of the absorber allows the absorbing Mössbauer nucleus to recoil with directional preference. Such an effect has been reported for iron^{57} embedded in a graphite lattice. The intensity of the Mössbauer effect is greater perpendicular to the graphite planes than parallel to them where the iron would have an enhanced opportunity to recoil (3).

The reports that the iron moves toward the carbinyl carbon in ferrocenyl carbonium ion (4) and, although only bonded to four carbons at a time, the iron rapidly moves around the entire π-system of cyclooctatetraene iron tricarbonyl (5) suggest that iron may possess an unusual freedom of motion in the plane of the π-ligands. It is therefore proposed that the iron nuclei of iron π-complexes in general, and ferrocene in particular, should be able to recoil more easily in directions

parallel to the planar organic ligand than perpendicular to the ligand, and that the Mössbauer effect of single crystals of these complexes should be greater in the perpendicular direction.

The existence of a difference in f along different crystallographic axes can be demonstrated in powdered samples; however, the value of f along a particular axis cannot be determined from such a sample (6). The Mössbauer effect reported for powdered π-cyclopentadienyl iron compounds indicate an anisotropy does exist, (7, 8) but the direction of the anisotropy has not been ascertained.

It remains merely to measure the Mössbauer effect along the different crystallographic axes.

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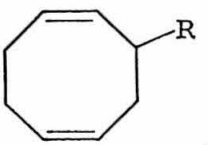
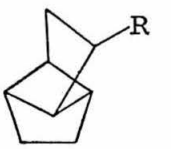
Proposition II

Several mechanisms have been proposed for the cuprous chloride catalyzed photoisomerization of 1,5-cyclooctadiene, Ia, to tricyclo-[3.3.0.$0^{2,6}$] octane, IIa (1,2). Srinivasan has reported that Ia forms



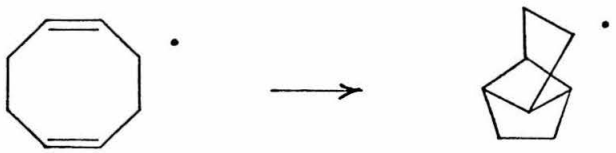
Ia R = H
Ib R = D
Ic R = Br



IIa R = H
IIb R = D
IIc R = Br

an isolatable 1:1 complex with cuprous chloride. However, he discounted the mechanistic possibility that photolysis of the complex may yield the tricyclooctane, IIa, directly, because the quantum yield for such a reaction must be of the order of 10 under his reaction conditions (1). He suggested that the incident light be absorbed by free cyclooctadiene, Ia, which then, while in an excited state, encounters a cuprous chloride molecule to effect isomerization. He determined that the quantum yield would be 0.1 for his suggested mechanism (1).

More recently, Baldwin has proposed that the isomerization proceeds via the radical intermediate, III, which rearranges to the tricyclo radical, IV. The radical, IV, would then abstract a hydrogen to form IIa (2). He based his proposal on a study of the cuprous chloride catalyzed photolysis of the deuterated cyclooctadiene, Ib. Photoisom-



III IV

erization of Ib produced roughly the statistically expected 87% monodeuterated IIb. However, a significant, but smaller, amount of deuterium was observed to be lost from recovered starting material (2).

It is proposed here that an excited diene–CuCl complex is, in fact, an intermediate in the photoisomerization, and that the two other mechanisms described above are incorrect.

The radical mechanism postulated by Baldwin seems questionable for the following reasons:

1. The reaction of Ia with N-bromosuccinimide to form Ic must involve the radical III as an intermediate, yet no tricyclo bromide, IIc, was observed among the products (3).
2. The mercury-sensitized (1) and ferrocene-sensitized (4) photolyses of Ia yield a preponderance of polymeric material in addition to small amounts of IIa, indicating that radical conditions favor the formation of polymer rather than IIa.

The deuterium labeling data can be explained if radicals in the reaction mixture abstract from IIa or IIb in preference to Ia or Ib. Baldwin rejects this possibility because the bond dissociation energy for a secondary alkyl carbon-hydrogen bond is about 94 kcal/mole while the corresponding dissociation energy for Ia → III is 82 kcal/

mole (2). However, if a concerted ring opening to III accompanies abstraction from IIa or IIb, the above argument should not hold. The radical mechanism can easily be tested by generating III in the presence of a hydrogen donor and looking for IIa among the reaction products.

Srinivasan's suggestion that an initially excited cyclooctadiene, Ia, encounters a molecule of cuprous chloride would require that a long-lived excited state of the diene (either singlet or triplet) diffuse to a cuprous chloride molecule before it initiates a polymerization reaction. The reports that both mercury-sensitized (1) and ferrocene-sensitized (4) photolyses of Ia yield mostly polymer make the existence of such an excited state seem unlikely in the cuprous chloride-sensitized photolysis.

The evidence reported (1) does not eliminate the possibility of a direct reaction of the diene-cuprous chloride complex. Since Srinivasan's irradiations used 2537 Å light (1), which is almost entirely absorbed by free diene, the high quantum yield that he observed can be explained if singlet transfer from Ia to the complex preceeds reaction of the complex. The singlet-transfer mechanism does not require a long-lived excited state of the diene as singlet energy transfer is known to occur over long distances in solution (5).

Measurement of the bulk quantum yield* of the reaction at 3130 Å, where the complex absorbs a greater proportion of the light, should provide a simple experimental test of this proposition. If the bulk

*In this proposition, "bulk quantum yield" will be defined as the number of molecules that react, divided by the number of protons absorbed by the entire solution.

quantum yield is greater at 3130 Å than at 2537 Å, this proposition would be supported since at 3130 Å a greater fraction of the incident light is used to excite the complex than at 2537 Å. The opposite result would support Srinivasan's suggestion.

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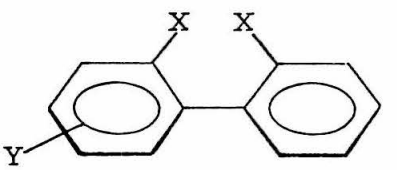
Proposition III

Melander and Carter have recently reported that substitution of deuterium for hydrogen at the 6 and 6' positions of 2, 2'-dibromo, 4, 4'-dicarboxybiphenyl enhances the rate of racemization of this compound (1). Mislow has observed a similar deuterium isotope effect on the racemization of 9, 10-dihydro, 4, 5-dimethylphenanthrene (2). The rate enhancement observed is attributed to less extensive steric interaction of bromine with deuterium than with hydrogen, because the carbon-deuterium bond length is shorter than the carbon-hydrogen bond length.

It is proposed that changing the Y substituent in 2, 2'-X, 4 or 5-Y biphenyl, I, (X is a substituent of sufficient size to make steric



I

resolution feasible) should exert an electronic effect upon the energy of activation for the racemization of these biphenyls. This substituent effect should alter the energy of the transition state in several ways. When Y is an electron-donating group, the electron density in the C_2-X and C_6-H bonds should be increased. Increased electron density leads to increased bond order and decreased bond length. An electron-donating group in the Y position would also increase the resonance between the rings when they are in the planar transition state. Both of the effects mentioned above tend to lower the energy of the transition state when Y is electron-donating. These effects lower the transi-

tion state energy because decreased C_2–X and C_6–H bond lengths lessen the steric barrier to rotation and because increasing the resonance interaction always lowers the energy. Electron-withdrawing groups should have an effect opposite to that of the electron-donating group.

Biphenyls substituted at 4 and 5 positions were chosen because little or no buttressing effects on the 6-hydrogen or 2-X group are expected (3). Therefore, the substituent effect should be entirely electronic in nature.

If we make the reasonable assumptions that the entropy of activation remains constant as Y is changed in I (Westheimer assumed that the entropy of activation of the 2,2'-dibromo and 2,2'-di-iodo 4,4'-dicarboxybiphenyls have similar entropies of activation (3), a much more daring assumption than ours) and the changes in the kinetic energy of the transition state are negligible as Y is varied (the change in kinetic energy is thought to be linearly related to the entropy of activation (4)), all of the conditions necessary for a linear free energy relationship are met. Such a relationship may then be anticipated. However, Hammett σ-meta and σ-para constants should not be expected to be ideal parameters for the biphenyl systems under consideration, since both meta and para effects are simultaneously operative. New σ constants must, therefore, be obtained. The other Hammett parameter, ρ, should be determined largely by the ability of the X substituent to interact with the ring. This ability should be largely a function of the electronic configuration of the X substituent.

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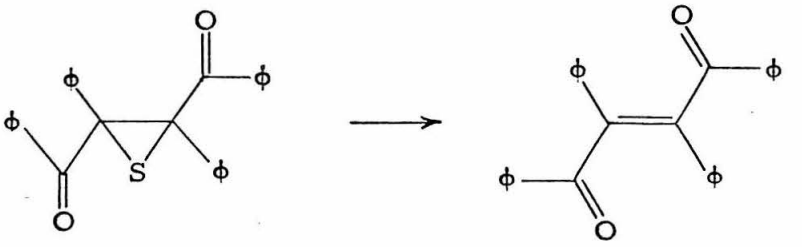
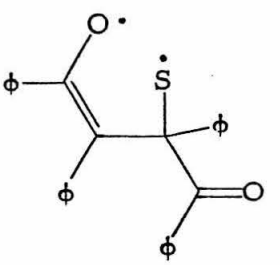
Proposition IV

Padwa and Crumrine have recently reported that the photolysis of trans-dibenzoylstilbene episulfide, I, produces trans-dibenzoylstilbene, II, with over 90% stereospecificity (1). Although thermal



I II

reactions of episulfides to form olefins have been reported to be stereospecific (2), one would not expect high stereospecificity for the photolysis of I, since both the excited intermediate, III, proposed by Padwa (1), and the electronically excited states of dibenzoylstilbene seem capable of rotation about the central carbon-carbon bond.

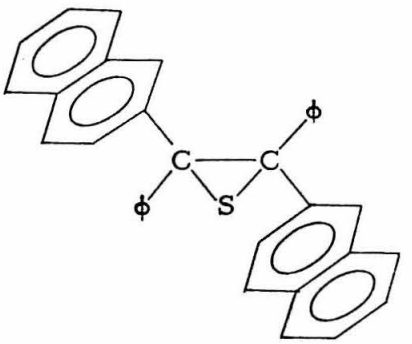


III

It is proposed that the reactive excited state is a triplet state of I which eliminates atomic sulfur as a ground state triplet to form the ground singlet state of II directly. The high intersystem-crossing

efficiencies reported for aromatic ketones (3) suggest that the intersystem-crossing efficiency of I is sufficiently high to produce the observed stereospecificity.

Comparison of the direct and sensitized photoelimination of episulfides such as IV, (and the corresponding cis isomer) which should not have so high an intersystem-crossing efficiency (3), should provide an experimental test of this proposition. If the proposed mechanism be correct, the sensitized photoelimination should be more stereo-



IV

specific than the direct photolysis.

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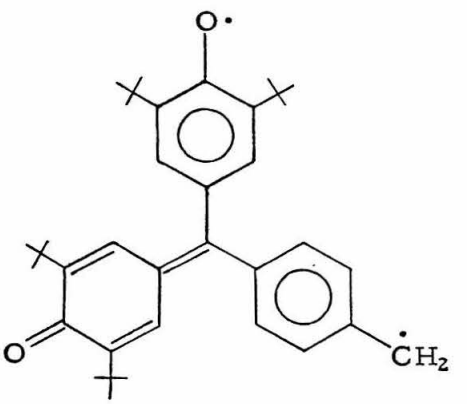
Proposition V

Bartlett (1) has recently reported a study of the cage recombination reaction of cumyl radicals formed by elevating azocumene to its excited singlet and triplet states. Although in the former case, cumyl radicals are presumably formed with paired electron spins, and in the latter case with unpaired electron spins, Bartlett observed no difference in the fraction of the radicals which underwent cage recombination. He attributed this observation to an apparently rapid spin relaxation process.

Spin relaxation of the electrons of methylene is sufficiently slow to allow experimental differentiation between the reactions of the singlet and the triplet states (2). It is, therefore, suggested that the rapid spin relaxation process observed by Bartlett occurs because the two radicals are sufficiently separated upon formation to prevent strong interactions between their electron spins. Each radical, then, approaches the approximation of a spin degenerate free radical in the absence of a magnetic field. In such a case, the degeneracy would be removed only as the two radicals in the cage approach each other during the coupling process. Since the radicals are assumed to be spin-degenerate at the inception of the approach, the spins they assume as they approach each other are independent of the spins they had upon formation. Presumably, they would approach in the manner that requires the least energy, i.e., with paired spins.

If the above model obtains, removing the spin degeneracy by providing a magnetic field to interact with the electron *spin might*

provide a means of keeping the cumyl radicals in their initial spin state long enough to experimentally discern a difference in the fraction of cage recombination product produced by triplet and singlet state azocumene. It is proposed that the degeneracy be removed by symmetrically substituting both rings of the azocumene with a stable free radical such as galvinoxyl (3) in the para positions. Bigalvinoxyl has been reported to be a stable triplet with interactions between the two unpaired electrons (4). Presumably, enough of these interactions would be present in the para-galvinoxylcumyl radical, I, to allow experimental verification of this proposition.



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